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THE

PHYSICAL REVIEW.

A STUDY OF APPARENT SPECIFIC VOLUME IN SOLUTION.

By LeRoy D. Weld.

I. Introduction.

THE research herein set forth had for its origin a desire to obtain further information as to the physical properties of dissolved substances when in very concentrated aqueous solution, that is, near the saturation point and even in the region of supersaturation. The percentage of ionization in such solutions being relatively low, it is reasonable to expect that the molecular properties of the solute will either resemble in large degree those of the pure substance in the liquid state, or else will be unique in some way and differ from those of the same solute in dilute solution.

The matter is here approached in one way only, perhaps the simplest. The immediate subject of the present paper relates to the volume of the solution as compared to the normal volume of the contained water, or what will be called the *apparent specific volume* of the dissolved solute; by which is meant, *the volume of the solution containing one gram of the solute, minus the natural volume of the pure water entering into it, at the same temperature.* The quantity just defined will be designated by Δ.

Δ will, of course, be generally less than the specific volume of the solid substance, sometimes very much less. In the case of potassium chlorate in saturated solution at ordinary temperatures, Δ is about 84 per cent. of the specific volume of the crystals, a ratio, it may be remarked, not differing very widely from that of the specific volume of liquid water and solid ice.

The values and variations of this quantity Δ under different circumstances and for different substances are here to receive attention. The first investigations relate to the variations of Δ with temperature at fixed concentration (what may be called the coefficient of expansion in solution), and the variations of Δ with concentration at fixed temperature.

II. Experimental Arrangements for Observing Continuous Change in Density of Solution.

Determinations of Δ will of course depend upon measurements of the density of the solution. It so happens that the excellent standard tables of physico-chemical data which are so useful for general purposes, such, for example, as Landolt and Börnstein, Castell-Evans, etc., do not give values of sufficient minuteness and precision for this purpose. In most of the work herein described, the probable errors of the measured densities are in the fifth decimal place, while the solution densities published in standard tables are usually given to the third or fourth place only.

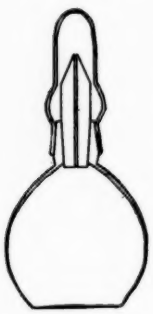


Fig. 1.

After considering and discarding in turn various forms of dilatometers and hydrometers, on account of the experimental difficulties involved in adapting them to highly precise absolute measurements with saturated solutions of accurately known concentration, the writer has adopted, as a standard, a specially designed pyknometer of the specific gravity bottle form and of about 25 c.c. capacity, shown in Fig. 1. The special features are (1) a tight-fitting glass cap, ground upon the neck of the bottle, which effectually prevents any measurable evaporation from neck and bore even after twenty-four hours in a desiccator; and (2) the conically pointed stopper, employed instead of the usual flat-topped stopper in order to prevent the formation of the overflow drop, which is so readily sucked in as the bottle cools after filling. The overflow immediately runs down the steep sides of the cone and cannot be sucked in.

Fig. 2.

In order to ensure still greater constancy of filling, the force with which the stopper is inserted is regulated and rendered uniform by means of a special instrument shown in Fig. 2. This is pressed down upon the conical stopper with the finger, against the spring, until the sharp point touches the finger, the overflow escaping through the slot in the side ofthe tube. The pressure on the stopper at this moment is about eight ounces.

In the process of filling, the liquid is placed in a closed jar or glass cell about 5 cm. in diameter, which is kept under precise thermostatic control. The open bottle is completely immersed in the liquid, where it remains for some time before being closed and removed. The stopper, held by a special clamp or handle, is also immersed in the liquid, so that all can come to the common temperature, indicated by a thermometer inserted

in the bottle, and reading to tenths of a degree. The conditions having become stable and uniform, the cell is uncovered and the bottle quickly stoppered. The stopper projects above the liquid surface, so that the pressure regulator can be applied. The bottle is now removed with another special forceps, quickly dried with desiccated gauze, and capped. When cool, it is ready for weighing.

The probable error of such a filling and weighing with this capped, cone-stoppered pyknometer has been found from a series of observations to be about 0.00025 g., or one-thousandth of one per cent., and is only half that with a flat-stoppered bottle similarly capped, the observations being therefore four times as reliable. The determination of Δ requires great absolute precision in the measurements of the density of the solution, and some of the earlier results, obtained with an ordinary specific gravity bottle loosely capped, were found later to be misleading.

Unusual care has to be exercised, also, in the weighing, since absolute results are required. To this end the balance resides permanently on a heavy pier in the center of a small room. The case is blanketed and otherwise shielded from temperature inequalities, as is very necessary,[1] and the pointer readings made at a moderate distance by means of a large collimating lens. Double weighings are always employed, the sensibility constants of the balance being determined with great care from time to time with standardized weights. The probable error of a single weighing has been found from several series of observations to be less than one millionth of the load. The vacuum correction is applied in the usual manner.

The dilatation constants of the pyknometer are also periodically determined by filling with water at different temperatures and weighing, as described above. Thus any gradual "creeping" of the glass with continued use is detected and eliminated from the results. Newly blown bottles are especially likely to exhibit such variations.

The stock solutions are carefully synthesized, of such strength as to become saturated at a predetermined temperature. They are made up one or two liters at a time and kept in tightly corked flasks. When desired for use, the flask is heated while still tightly closed until the crystals dissolve, and then cooled to about the required temperature, the specimen being then quickly removed to the closed thermostatic cell. The stock solutions are not exposed to evaporation for more than a few seconds during their entire history, and therefore remain very nearly constant.

All the earlier work was done directly by the pyknometer method

[1] Weld, Iowa Academy of Science, Proc., 1909, Vol. 16, p. 181.

above described, and it is hardly necessary to say that it was very tedious. Every point on the Δ curve represented a separate specimen from the stock solution and a filling and weighing of the pyknometer (an operation requiring from half to three-quarters of an hour), so that only a few points could be obtained in an afternoon's work.

In order to replace this slow process by a sufficiently reliable one that would be quicker and at the same time more nearly continuous in its indications of Δ, the writer has resorted to an Archimedes principle method, which may be called the *secondary* method, dependent upon the absolute pyknometer method as a *primary* standard of accuracy. The sinker consists of a loaded glass bulb of about 34 c.c. volume and weighing about 50 g. suspended from the balance beam by a very fine platinum wire. When immersed in the solution, and counterpoised with weights, this arrangement acts as a very sensitive hydrometer, whose scale is represented jointly by the weights and the balance pointer scale. A change of temperature of one degree is accompanied by an alteration of as much as ten to fifteen milligrams in buoyancy. This change is of course neutralized to the nearest milligram by the addition or removal of weights, the fractional milligram being then read off as a slight deflection on the pointer scale from the known sensibility constants. The rider has not been resorted to in any of the work, except as a means of adjusting the pointer to zero at the outset of each experiment. The pointer has to be read stationary, not by oscillations, as the viscosity of the solution quickly damps out the oscillations.

The sinker, like the pyknometer, has been accurately calibrated for dilatation by immersing in pure water of varying temperature. The standardization presently to be explained may possibly render this unnecessary, but it has been thought best to make the secondary method as nearly absolute as practicable without sacrificing its convenience.

A more immediate reason, even than that of labor-saving, for adopting the secondary method, was the fact that it involves much less disturbance of the liquid under examination, and is therefore better adapted to use with supersaturated solutions, which are likely to begin crystallizing out if agitated. The sinker hangs very quietly in the liquid, which is examined at short intervals in a strong beam of light; and when crystals begin to form, they are immediately detected and the work stopped.

The principal sources of discrepancy between the secondary and absolute measurements lie (1) in the impossibility of double weighings in the former, and hence the entrance into the results of the balance arm-ratio (which differs on different days and often shows a slow progressive variation even in the course of a few hours' work); and (2) in the un-

certain capillary force acting upon the platinum suspension wire at the surface of the liquid. It is also difficult to get the depth of solution above the sinker quite constant, so that the amount of the fine wire immersed is slightly variable in different experiments.

The reduction of the secondary results to absolute measure is made by means of corresponding values of the specific volume *of the solution*, this being the first stage reached in common by the two methods. This process may be illustrated by the following example.

A near-saturated solution of potassium chlorate was being experimented upon. The specific volumes of the solution obtained from a typical series of sinker observations are here tabulated along with corresponding pyknometer determinations for certain temperatures.

Temp.	Sinker Method.	Pyknometer Method.	Calculated Absolute.
°			
23.0	0.952750		0.952839
23.5	0.952879		0.952982
24.0	0.953003		0.953121
24.5	0.953177	0.953322	0.953316
25.0	0.953339	0.953488	0.953497
25.5	0.953505		0.953683
26.0	0.953678		0.953876
26.5	0.953840	0.954059	0.954057
27.0	0.954012		0.954249
27.5	0.954187		0.954446
28.0	0.954366		0.954646
28.5	0.954526		0.954824
29.0	0.954701		0.955020
29.5	0.954872		0.955212
30.0	0.955075		0.955438
31.0	0.955426		0.955831

The values in the second column constitute the secondary series of specific volumes taken with the sinker, and involve all the persistent errors inherent in the method. Each of the three determinations in the third column is the mean of three careful measurements with the pyknometer, and these may be considered as "tie points," to be used in reducing the secondary series to absolute measure. This "tying in" process is as follows.

Let X = a secondary result at any temperature,

Y = the corresponding absolute result desired.

Assume the simple linear relation $Y = AX + B$ as the basis of the observation equations which are to connect the series. There will be as many of these equations as there are absolute data available, in this case three.

Least square adjustment (which need be here applied only to the last four decimal places), now gives the constants A and B, and the transformation formula with these values inserted becomes for this case

$$Y = 1.1183\,X - 0.112622.$$

The adoption of such a simple linear relation is justified by the small values of the discrepancies to be eliminated. The absolute specific volumes thus calculated are given in the last column of the table, and the whole process is shown graphically on the accompanying diagram, Fig. 3. The "tie points" in this particular case were taken too near

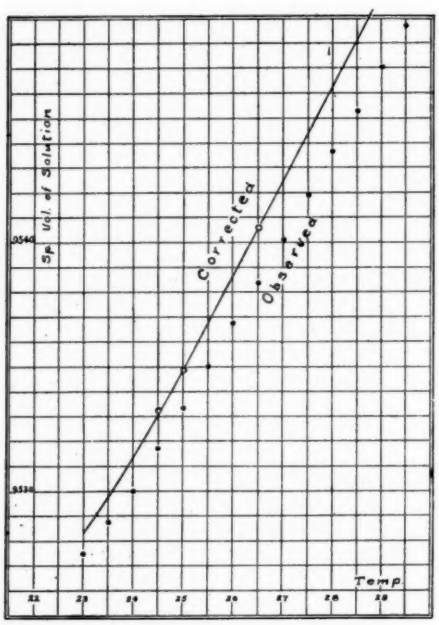


Fig. 3.

together. They have usually been chosen as far apart as possible, but they cannot enter the region of supersaturation on account of the formation of crystals in the pyknometer.

For the study of the behavior of Δ at given concentration over any particular temperature range, several such series as the above may be made in a short time (each series taking but one specimen from the stock solution), the series weighted, averaged and standardized, and the corresponding Δ series then calculated from the known concentration and the known specific volumes of pure water.

III. RESULTS WITH POTASSIUM CHLORATE.

The only substance with which complete series have been obtained up to the present time is potassium chlorate, but experiments are now in progress along similar lines, in which copper sulphate, sodium carbonate, sodium sulphate and possibly other solutes are to be examined, the results to be published later in a separate paper. The results with potassium chlorate are, however, in certain respects so singular, as to lead the writer to present them at this stage.

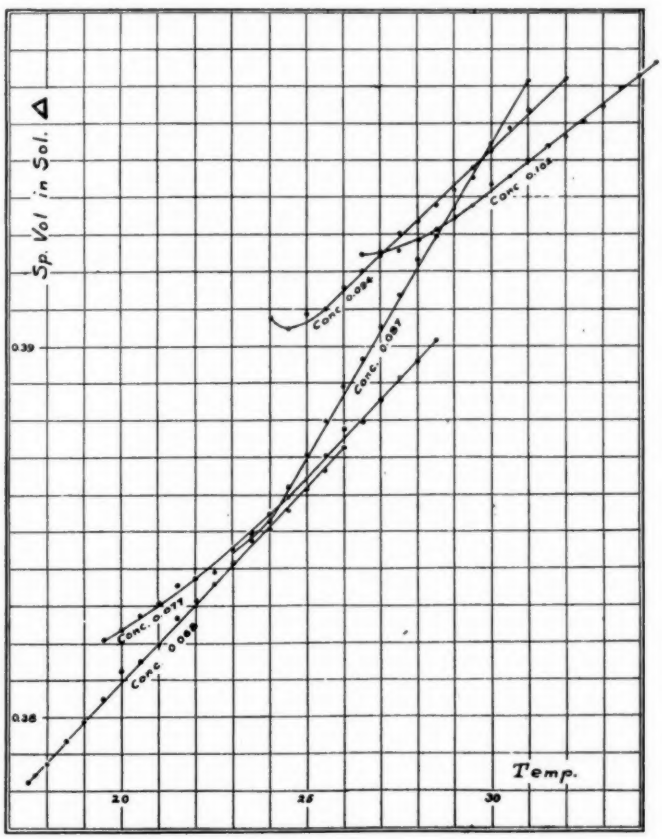


Fig. 4.

Potassium chlorate is rather sparingly soluble in water, about 7 per cent. dissolving at 20° C. The solubility rapidly increases with temperature, the heat of solution and hence the constant B of the solubility equation being large. This gives a sharply defined saturation, which is advantageous in some ways and in others not so. The other salts mentioned are much more soluble and saturation is less distinct.

In Fig. 4 are shown typical curves for potassium chlorate, in which abscissas represent temperature and ordinates the apparent specific volume in solution, Δ. The concentration is indicated for each curve. Concentrations are expressed in grams of solute per gram water.

In each of the curves except that for the most dilute solution, there is a distinct upward concavity and an unmistakable suggestion of approaching a minimum as the temperature is lowered. A minimum actually appears in the curve for concentration 0.094, and there is indication that it would be reached in the others if the experiment could be extended far enough into the region of supersaturation, which was successfully accomplished only in the one case. The saturation temperature for this concentration is about 27°.5, or three degrees above the minimum indicated by the curve.

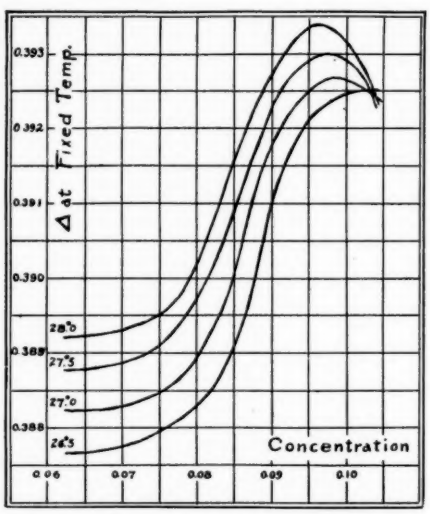


Fig. 5.

The significance of this concavity in the curves, and of the minimum if it really exists, is very interesting, for it suggests at once the behavior of pure water just before it crystallizes on cooling, and of impure water (as a weak solution of salt) when supercooled. It is well known that the minimum volume point, which is at 4° for pure water, is lowered by the addition of a solute, and soon passes below the freezing point of the solution, so as not to be attained except by supercooling. Now if we could interchange the relations of solute and solvent, and regard a concentrated solution as merely a mixture of two substances both in the fused condition (though below their pure melting points), we might regard this observed behavior of potassium chlorate mixed with water as

analogous to that of water mixed with salt, and explain it by something akin to Roentgen's ice molecule hypothesis. This would also be in agreement with the fact that, the more impurity (water) there is mixed with the substance under examination (potassium chlorate), the farther below the crystallizing (saturation) point of the latter does the minimum specific volume appear to be, which is evident from an examination of the curves.

The second interesting feature of these results is the variation of Δ with concentration at a fixed temperature, obtained from the same series of experiments. This is shown typically by the curves in Fig. 5, each of which pertains to a single temperature.

It was expected that there would be, for each temperature, a more or less uniform change in Δ with concentration. On the contrary, we observe at 26°.5, for example, a sudden increase in the neighborhood of

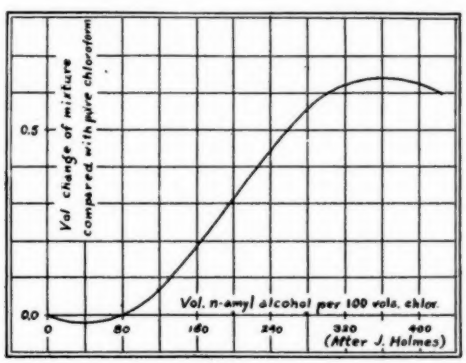


Fig. 6.

concentration 0.087, giving a point of inflection; while for the higher temperatures, furthermore, Δ goes through a very pronounced maximum for concentrations between 0.095 and 0.100. For this phenomenon the writer has, as yet, no explanation to suggest. It is interesting to compare these results with those obtained by J. Holmes[1] on the volume of a mixture of *n*-amyl alcohol in chloroform. As the percentage of the alcohol, as compared with the chloroform, increases, the volume of the mixture goes through a minimum and then a maximum with a point of inflection between (Fig. 6), the curve being somewhat suggestive of some of the curves of Fig. 5. Probably a separate research, arranged along somewhat different lines of procedure, might be profitably directed toward this question.

[1] J. Holmes, Intermiscibility of Liquids, Chem. Soc. Jour., 103, Dec., 1913.

In conclusion, attention may be called to the very large apparent coefficient of expansion of potassium chlorate in solution, that is, the rapid fractional increase of Δ with temperature, as indicated by the slopes of the curves in Fig. 4. This is seen to be especially large for concentration 0.087, and the average apparent volume coefficient per centigrade degree for all the concentrations tested, taken outside the neighborhood of the minimum volume, is about 0.0029, a value more than fifteen times the volume coefficient of expansion of mercury and about four-fifths that of a perfect gas.

Very little physical significance can, however, be attached to these latter figures, inasmuch as the quantity Δ is defined in an arbitrary manner, without any reference to the possible shrinkage of the water itself when the salt is dissolved in it,[1] which would make the actual value of the volume of the salt in solution larger than Δ by an unknown amount. The point is that, while Δ itself represents something quite uncertain, the *changes* in Δ here observed undoubtedly do represent some physical process peculiar to the solute and probably connected with its molecular structure. In what manner this process depends upon the dissolved substance, may appear more clearly when other substances have been similarly experimented upon.

I desire to acknowledge my indebtedness to Mr. M. H. Teeuwen, of the University of Iowa, for assistance in constructing certain parts of the apparatus, and to several of my students, whose painstaking co-operation proved very helpful in the experimental work.

COE COLLEGE,
CEDAR RAPIDS, IOWA,
June, 1915.

[1] W. F. Magie, PHYS. REV., Vol. 18, p. 449.

THE HEAT LOSSES FROM INCANDESCENT FILAMENTS IN AIR.

BY L. W. HARTMAN.

IN a former paper by the writer[1] the heat losses from a hot black body in air were determined and on the assumption that the Stefan-Boltzmann law held for the radiation, the law governing the conduction and convection losses was deduced. During the past two years several new determinations of the constant of radiation, σ, in the relation

$$E = \sigma(T^4 - T_0^4)$$

of the Stefan-Boltzmann law have been published. The value of 5.61×10^{-12} watt cm.$^{-2}$ degree^{-4} for σ, given by Coblentz in a recent communication,[2] seems to be the best determination made thus far, although Gerlach[3] defends with considerable vigor his determination, where $\sigma = 5.90 \times 10^{-12}$ watt cm.$^{-2}$ degree^{-4}. It appeared therefore that a new computation and study of the heat losses from small hot rods in air and the graphs obtained from these data would prove of interest and value, and might serve to indicate which was the most probable value of the constant mentioned.

The method of obtaining the data was as follows: Wires of platinum sponge varying in size from 0.2 mm. to 0.7 mm. in diameter served as black bodies. On the ends of these were fused terminals of silver wire. These wires were then mounted in front of an electric furnace at the center of which was mounted a piece of magnesium oxide. This furnace consisted of an unglazed porcelain tube, 10–15 cm. long and 1 cm. in diameter, over which was wrapped, as the heater, a layer of platinum wire, and the whole was surrounded by a thick layer of plaster paris so as to fill a large glass cylinder in which this combination was mounted with the axes of the tube and cylinder coincident.

The temperature of the furnace was measured with a thermo-couple embedded in the magnesium oxide and with a Wanner pyrometer. These two series of temperature measurements were found to be in close accord. The wires serving as black bodies were then mounted in front

[1] Physikalische Zeitschr, 5, 576, 1904.

[2] Bull. Bureau Standards, 11, 87, 1914.

[3] Ann. der Phys. (4), 38, 1, 1912; 40, 701, 1913; 41, 99, 1913; 42, 1163, 1167, 1913.

of the electric furnace so that they had the piece of magnesium oxide for a background. By means of a current from a storage battery the wires were heated until they seemed to have the same temperature as the interior of the furnace. This was determined by observing the interior of the furnace through a telescope when the wire could be seen against the heated block of magnesium as a background. As the current through the wire was varied a point was finally attained where the incandescent wire disappeared from view. On the principle on which the Holborn-

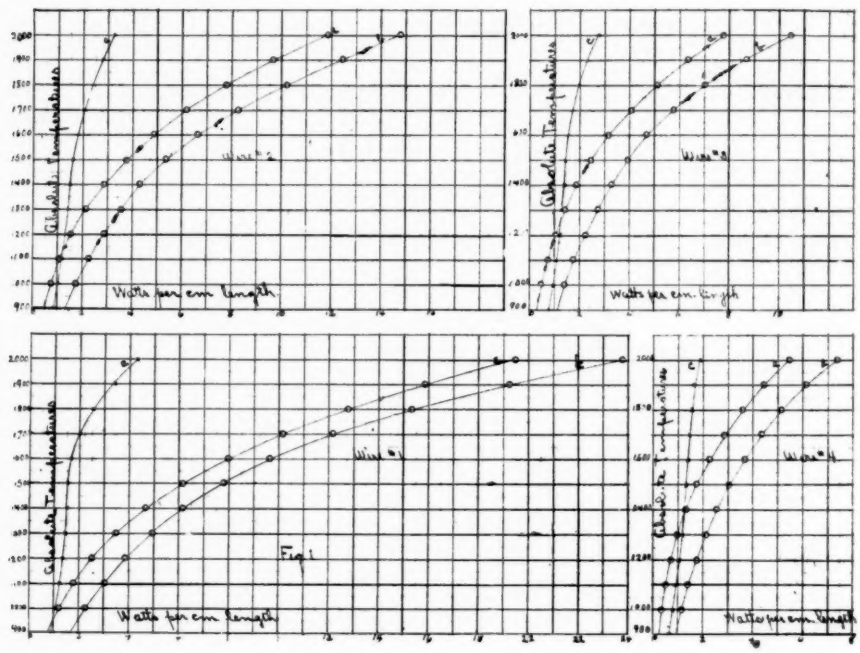


Fig. 1.

Kurlbaum pyrometer is based, the wire and the oxide at this point were assumed to have the same temperature. The temperature of the furnace was then determined by means of the pyrometer, and the current supplied to the black body was read on an ammeter in series with the wire and the voltage across its terminals was determined by means of a voltmeter. Thus, readings of power and temperature were obtained for temperatures ranging approximately from 700° C. to 1700° C.

With the data thus obtained curves were then plotted with absolute temperatures as ordinates and power, expressed in watts per centimeter length, supplied to the wire as abscissæ. From these curves the values of the watts supplied to the wires to produce absolute temperatures of 900, 1000, . . . 2000° Absolute could be determined. Using the Co-

blentz value of σ, indicated above, and the Stefan-Boltzmann law, the energy radiated by a black body having the same dimensions as those of the wire used, was computed. The difference between these two values for a given wire represents the loss due to convection and conduction at the given temperature. These values are shown in Table I. In a similar manner the same quantities based upon Gerlach's determination of σ, were computed, but owing to lack of space are not shown here.

If now one should plot for each wire, from the data contained in Table I., a series of curves with absolute temperatures for ordinates and computed watts per centimeter, measured watts per centimeter, and watts per centimeter lost in air, respectively, as abscissæ he would obtain the curves a, b, c, shown in Fig. 1. Plotting the curves marked c for all four wires to a larger scale upon one sheet it will be found that the curves based upon Coblentz's determination of σ are more symmetrical than those based upon Gerlach's value. The losses per square millimeter for each wire, based on the respective values of σ mentioned above were then computed and the curves obtained from these data are shown in Fig. 2.

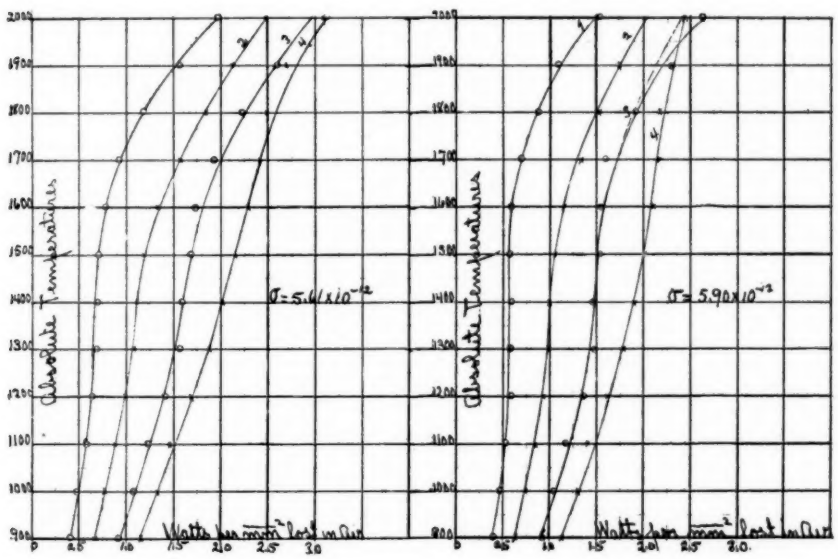


Fig. 2.

Again the curves based on Coblentz's determination of the value of the radiation constant are more symmetrical and uniform than those based on Gerlach's determination of this constant. In the fifth division of Table I. are given the values of the ratio of the watts per centimeter length of wire to the absolute temperature. It will be observed that

TABLE I.

$\sigma = 5.61 \times 10^{-12}$ watt cm.$^{-2}$ deg.$^{-4}$

Computed Radiation in Watts per Centimeter.

Diameters in Cm.	Absolute Temperatures.											
	900	1000	1100	1200	1300	1400	1500	1600	1700	1800	1900	2000
1. .0690	.79	1.21	1.78	2.52	3.47	4.67	6.16	7.97	10.15	12.77	15.85	19.45
2. .0420	.48	.73	1.09	1.53	2.11	2.84	3.74	4.84	6.17	7.77	9.65	11.85
3. .0275	.32	.48	.71	1.01	1.38	1.86	2.45	3.17	4.05	5.09	6.32	7.75
4. .0194	.22	.34	.50	.71	.97	1.31	1.73	2.24	2.85	3.59	4.46	5.47
Watts per Centimeter Observed.												
	1.70	2.26	3.01	3.88	4.92	6.18	7.70	9.63	12.15	15.33	19.25	23.75
	1.35	1.75	2.26	2.84	3.53	4.29	5.33	6.60	8.25	10.20	12.45	14.75
	1.12	1.40	1.76	2.23	2.73	3.23	3.91	4.67	5.72	7.00	8.64	10.45
	.92	1.15	1.39	1.74	2.12	2.54	3.04	3.64	4.32	5.10	6.10	7.35
Watts per Centimeter Lost in Air.												
	.91	1.05	1.23	1.36	1.45	1.51	1.54	1.66	2.00	2.56	3.40	4.30
	.87	1.02	1.17	1.31	1.42	1.45	1.57	1.76	2.08	2.43	2.80	3.26
	.80	.92	1.05	1.22	1.35	1.37	1.46	1.50	1.67	1.91	2.32	2.70
	.70	.81	.89	1.03	1.15	1.23	1.31	1.40	1.47	1.51	1.64	1.88
Watts per Sq. Mm. Lost in Air.												
	.42	.48	.57	.63	.67	.69	.71	.77	.92	1.18	1.57	1.98
	.66	.77	.89	.99	1.08	1.10	1.18	1.33	1.58	1.84	2.12	2.47
	.92	1.06	1.22	1.41	1.56	1.58	1.69	1.73	1.94	2.21	2.58	3.12
	1.15	1.33	1.46	1.69	1.89	2.02	2.16	2.30	2.41	2.48	2.69	3.08
(Watts per Centimeter Lost in Air ÷ Absolute Temperature) ×10⁶.												
Mean.[1]	900	1000	1100	1200	1300	1400	1500	1600	1700	1800	1900	2000
1,092	1,011	1,050	1,118	1,133	1,115	1,080	1,027	1,038	1,178	1,420	1,789	2,150
1,083	967	1,020	1,062	1,091	1,091	1,035	1,047	1,100	1,222	1,350	1,472	1,630
976	889	920	955	1,017	1,039	979	973	938	983	1,060	1,220	1,350
854	780	810	810	858	887	879	874	875	865	840	863	940
(Watts per Sq. Mm. Lost in Air ÷ Absolute Temperature) ×10⁶.												
498	466	480	520	525	515	493	474	480	530	655	826	990
811	735	770	810	825	830	785	786	831	930	1,022	1,118	1,235
1,115	1,030	1,060	1,109	1,173	1,200	1,130	1,125	1,080	1,140	1,230	1,360	1,560
1,394	1,280	1,330	1,327	1,408	1,455	1,445	1,440	1,439	1,420	1,380	1,417	1,540

between 900–1700° Absolute these ratios for a given wire are approximately constant. Hence we may say that the energy loss per centimeter length of wire through conduction and convection, (L), within this range

[1] These means are taken between 1000–1700° Absolute.

of temperature, is proportional to the absolute temperature, (T). This law may be expressed by the equation

$$L = kT,$$

where k has the value shown in the table. The last division of Table I. shows the values of the ratio watts per square millimeter lost in air to absolute temperature. As one would expect between 900–1700° Absolute these ratios for a given wire are constant and in each case the mean value of this constant within the range specified is shown in the column to the left. It may be noted here, however, that the energy loss per centimeter length of wire due to convection and conduction can be expressed approximately by the relation

$$L = 0.0010T,$$

where the wires range between 0.2–0.7 mm. in diameter.

In order to separate the conduction and convection losses, the effect of enclosing the wires in a vacuum was then tried. In a glass vessel of suitable form having a ground glass cork provided with a mercury seal each wire in turn was mounted so that the wire was in front of the electric furnace as mentioned above. With a mercury pump the air was exhausted from this vessel, a current of electricity was passed through the wire for some time and the vessel again pumped out until after several repetitions of this process a relatively high vacuum was obtained. The vessel was then sealed off. The energy and temperature measurements previously indicated were then repeated. The difference between the watts per centimeter length as observed and the watts per centimeter length as computed from the Stefan-Boltzmann law for each wire gives the losses due to conduction. The watts per centimeter length supplied to each wire for given temperatures were determined when the wires were mounted within the vessel but with the seal broken and then when the wires were mounted in the open air outside the vessel. From the curves plotted for these two series of observations, correction can be made for the absorption of the glass of the vessel. These curves showing the absorption by the glass vessel are given in Fig. 3. It will be observed that the loss increases with the rise of temperature, and of course increases with the increase in diameter of the wire. The difference between the total energy loss and the sum of the radiation and conduction losses, the two being corrected for the absorption of the glass vessel, gives the convection loss. This loss for each wire at the temperature specified is given in Table II., the data in the first division of which are based on the lower value of σ and in the second division on the higher value of this constant. Fig. 3 shows graphically the results for the first division of Table II.

In the second section of Division II. of Table II., it may be noted that the conduction losses in watts per centimeter decrease with rise of temperature for the smallest wire. This is not true in the corresponding section of Division I. of the same table. From this one might infer that

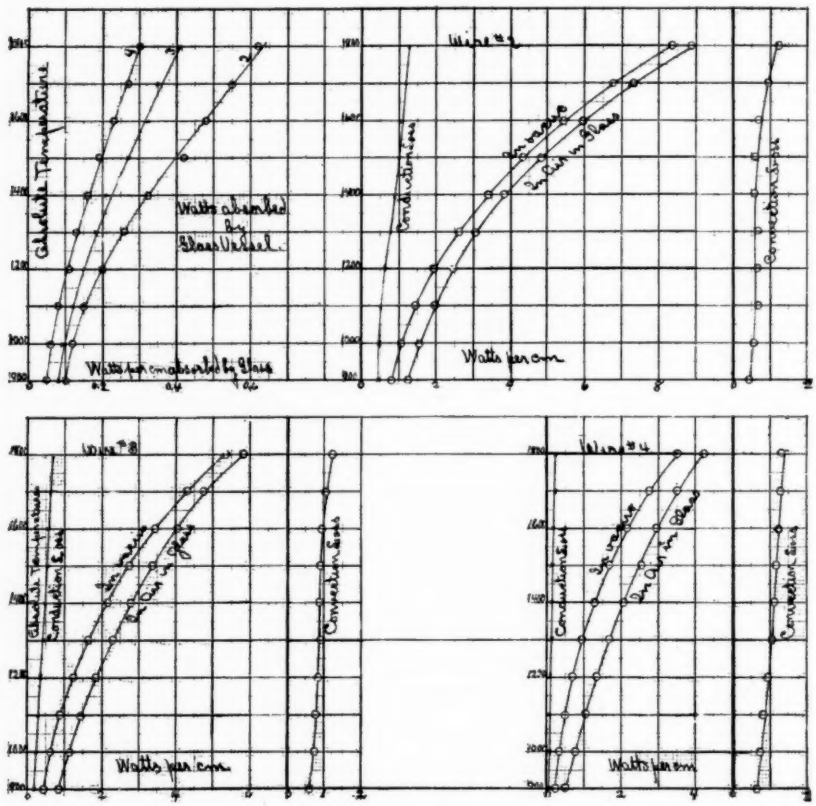


Fig. 3.

5.90×10^{-12} watt cm.$^{-2}$ degree^{-4} is too high a value for the constant σ; in fact, one is even inclined to believe that 5.61×10^{-12} watt cm.$^{-2}$ degree^{-4} is as high as, or even higher than, these data justify.

Lorenz[1] has developed a formula for the energy absorbed by a wire when heated in air. His equation takes the form

$$E' = A(T^4 - T_0^4) + B(T - T_0),^{5/4}$$

where E' is the energy absorbed, T is the absolute temperature of the wire, T_0 is the room temperature on the absolute scale, and A and B are constants. If we use the method of least squares and apply it to the

[1] Wied. Ann., 13, 582, 1881.

TABLE II.

$\sigma = 5.61 \times 10^{-12}$.

Division I. Computed Radiation in Watts per Centimeter.

Wire No.	Diameter in Cm.	Absolute Temperatures.									
		900	1000	1100	1200	1300	1400	1500	1600	1700	1800
2.	.0420	.48	.73	1.09	1.53	2.11	2.84	3.74	4.84	6.17	7.77
3.	.0275	.32	.48	.71	1.01	1.38	1.86	2.45	3.17	4.05	5.09
4.	.0194	.22	.34	.50	.71	.97	1.31	1.73	2.24	2.85	3.59
		Observed Watts per Cm. in Vacuum in Glass Vessel.									
		.80	1.07	1.43	1.94	2.60	3.40	4.32	5.43	6.75	8.37
		.42	.60	.87	1.21	1.63	2.13	2.73	3.42	4.30	5.35
		.23	.36	.50	.69	.95	1.27	1.68	2.16	2.76	3.50
		Observed Watts per Cm. in Air in Glass Vessel.									
		1.25	1.55	1.95	2.46	3.05	3.83	4.82	5.96	7.30	8.85
		.82	1.11	1.44	1.83	2.30	2.79	3.36	4.03	4.76	5.80
		.50	.75	1.02	1.33	1.67	2.04	2.55	2.94	3.50	4.22
		Watts Absorbed by Glass Vessel.									
		.10	.12	.15	.20	.26	.32	.42	.48	.55	.62
		.08	.09	.12	.15	.18	.21	.27	.32	.35	.41
		.05	.06	.08	.11	.13	.16	.19	.23	.27	.30
		Conduction Loss in Watts per Cm.									
		.42	.46	.49	.61	.75	.88	1.00	1.07	1.13	1.22
		.18	.21	.28	.35	.43	.48	.55	.57	.60	.67
		.06	.08	.08	.09	.11	.12	.14	.15	.22	.23
		Convection Loss in Watts per Cm.									
		.45	.56	.68	.70	.67	.57	.59	.69	.95	1.21
		.62	.71	.77	.87	.92	.89	.91	.93	1.07	1.24
		.64	.73	.81	.94	1.04	1.11	1.17	1.25	1.29	1.30

$\sigma = 5.90 \times 10^{-12}$.

Division II. Computed Radiation in Watts per Centimeter.

		.51	.77	1.14	1.61	2.22	2.98	3.94	5.10	6.49	8.19
		.33	.50	.75	1.06	1.46	1.96	2.58	3.34	4.25	5.35
		.23	.36	.53	.75	1.03	1.38	1.82	2.36	3.00	3.78
		Conduction Loss in Watts per Cm.									
		.39	.42	.44	.53	.64	.74	.78	.81	.81	.80
		.13	.18	.24	.30	.35	.38	.42	.40	.40	.41
		.05	.06	.05	.05	.05	.05	.05	.03	.03	.04
		Convection Loss in Watts per Cm.									
		.45	.56	.68	.70	.67	.57	.57	.69	.95	1.21
		.66	.71	.77	.87	.92	.89	.91	.93	1.07	1.24
		.64	.73	.81	.94	1.04	1.11	1.17	1.25	1.29	1.30

data for wire No. 1 as contained in the second part of Table I., we obtain $A' = 1.12 \times 10^{-12}$ and $B' = 3.035 \times 10^{-4}$. Tereschin[1] makes the assumption that the constant A in the above equation is proportional to the surface of the wire and therefore for a unit length of wire is proportional to the diameter of the wire. On this basis one can compute the values of A and B for each wire. Thus one obtains:

TABLE III.

Wire No. 1.							Wire No. 2.					
T Abs.	E Obs.	E' Comp.	S Comp.	Energy Losses. $E'-S$	L Obs.	$L=kT$ Comp.	E Obs.	E' Comp.	S Comp.	Energy Losses. $E'-S$	L Obs.	$L=kT$ Comp.
900	1.70	1.66	.74	.92	.91	.98	1.35	1.20	.45	.85	.87	.97
1,000	2.26	2.22	1.11	1.11	1.05	1.09	1.75	1.71	.68	1.03	1.02	1.08
1,100	3.01	2.94	1.63	1.31	1.23	1.20	2.26	2.21	.99	1.22	1.17	1.19
1,200	3.88	3.84	2.32	1.52	1.36	1.31	2.84	2.82	1.41	1.41	1.31	1.30
1,300	4.92	4.93	3.20	1.73	1.45	1.42	3.53	3.56	1.95	1.61	1.42	1.41
1,400	6.18	6.24	4.30	1.94	1.51	1.53	4.29	4.43	2.62	1.81	1.45	1.52
1,500	7.70	7.72	5.66	2.06	1.54	1.64	5.33	5.45	3.44	2.01	1.57	1.63
1,600	9.63	9.75	7.35	2.40	1.66	1.75	6.60	6.69	4.47	2.22	1.76	1.73
1,700	12.15	11.97	9.35	2.62	2.00	1.86	8.25	8.13	5.69	2.44	2.08	1.84
1,800	15.33	14.60	11.75	2.85	2.56	1.97	10.20	9.85	7.17	2.68	2.43	1.95
1,900	19.25	17.69	14.60	3.09	3.40	2.08	12.45	11.76	8.90	2.86	2.80	2.06
2,000	23.75	21.24	17.90	3.34	4.30	2.18	14.75	13.99	10.89	3.10	3.26	2.17
Wire No. 3.							**Wire No. 4.**					
900	1.12	1.05	.29	.76	.80	.88	.92	.84	.21	.63	.70	.77
1,000	1.40	1.46	.44	.92	.92	.98	1.15	1.08	.31	.77	.81	.85
1,100	1.76	1.73	.65	1.08	1.05	1.07	1.39	1.38	.46	.92	.89	.93
1,200	2.23	2.18	.93	1.25	1.22	1.17	1.74	1.70	.65	1.05	1.03	1.02
1,300	2.73	2.71	1.28	1.43	1.35	1.27	2.12	2.10	.90	1.20	1.15	1.11
1,400	3.23	3.32	1.72	1.60	1.37	1.37	2.54	2.55	1.21	1.34	1.23	1.19
1,500	3.91	4.04	2.26	1.78	1.46	1.46	3.04	3.09	1.59	1.50	1.31	1.28
1,600	4.67	4.90	2.93	1.97	1.50	1.56	3.64	3.72	2.06	1.66	1.40	1.37
1,700	5.72	5.90	3.74	2.16	1.67	1.66	4.32	4.44	2.63	1.81	1.47	1.45
1,800	7.00	7.05	4.70	2.35	1.91	1.76	5.10	5.28	3.31	1.97	1.51	1.54
1,900	8.64	8.37	5.82	2.55	2.32	1.86	6.10	6.25	4.11	2.14	1.64	1.62
2,000	10.45	9.90	7.15	2.75	2.70	1.95	7.35	7.36	5.05	2.31	1.88	1.71

$A' = 1.120 \times 10^{-12}$ $\quad B' = 3.035 \times 10^{-4}$

$A'' = .682 \times 10^{-12}$ $\quad B'' = 2.820 \times 10^{-4}$

$A''' = .447 \times 10^{-12}$ $\quad B''' = 2.500 \times 10^{-4}$

$A'''' = .315 \times 10^{-12}$ $\quad B'''' = 2.100 \times 10^{-4}$

Lorenz's Formula:—$E = A(T^4 - T_0^4) + B(T - T_0)^{\frac{5}{4}}$

[1] Physikalische Zeitschr., 6, 217, 1905.

$$A'' = 0.682 \times 10^{-12},$$
$$AA''' = 0.447 \times 10^{-12},$$
$$A'''' = 0.315 \times 10^{-12}.$$

Having thus obtained the values of A for the different wires one can compute for each of the absolute temperatures given in the table the values of the first term in the second member of Lorenz's equation, which may be designated by S, as follows:

$$S = A(T^4 - T_0^4).$$

The difference between the observed energy supplied to each wire and the value of S gives us

$$E - S = B(T - T_0)^{5/4}.$$

These values are given in Table IV. The mean values between 900–1700° Absolute and 900–2000° Absolute are also indicated in this table.

TABLE IV.

Computation of B in Lorenz's Formula.

T	E Obs.	$E-S$	$B''\times10^{-4}$ Comp.	E Obs.	$E-S$	$B'''\times10^{-4}$ Comp.	E Obs.	$E-S$	$B''''\times10^{-4}$ Comp.
900	1.35	.90	2.96	1.12	.83	2.74	.92	.62	2.05
1,000	1.75	1.07	2.92	1.40	.96	2.62	1.15	.84	2.29
1,100	2.26	1.27	2.94	1.76	1.11	2.57	1.39	.93	2.15
1,200	2.84	1.43	2.86	2.23	1.30	2.60	1.74	1.09	2.18
1,300	3.53	1.58	2.78	2.73	1.45	2.74	2.12	1.22	2.14
1,400	4.29	1.67	2.61	3.23	1.51	2.36	2.54	1.33	2.08
1,500	5.33	1.89	2.65	3.91	1.65	2.32	3.04	1.45	2.04
1,600	6.60	2.13	2.70	4.67	1.74	2.21	3.64	1.58	2.00
1,700	8.25	2.56	2.96	5.72	1.98	2.29	4.32	1.69	1.96
1,800	10.20	3.03	3.22	7.00	2.30	2.44	5.10	1.79	1.90
1,900	12.45	3.55	3.48	8.64	2.82	2.76	6.10	1.99	1.95
2,000	14.75	3.86	3.51	10.45	3.30	3.00	7.35	2.30	2.09
Mean (900–1,700)			2.82			2.50			2.10
Mean (900–2,000)			2.97			2.55			2.07

A'', A''', A'''', respectively, have the values given in Table III.

Taking the mean value of B between 900–1700° Absolute and the corresponding value of A shown above, from Lorenz's equation one can compute for each wire the energy (E') required to produce a given temperature. These values are also shown in Table III. The quantity S, in this table represents, as mentioned above, the first term in the second member of Lorenz's equation. Hence the columns labeled $E'-S$ should equal the losses due to conduction and convection. Under the

heading Energy Losses in Table III. are given the quantities just mentioned, the observed values of the conduction and convection losses as given in the third section of Table I., and the losses as computed from the equation

$$L = kT.$$

It will be observed that the deviation between 900–1700° Absolute from the observed loss as computed from this latter equation is less than is the quantity $(E' - S)$ between the same limits of temperature computed by Tereschin's method.

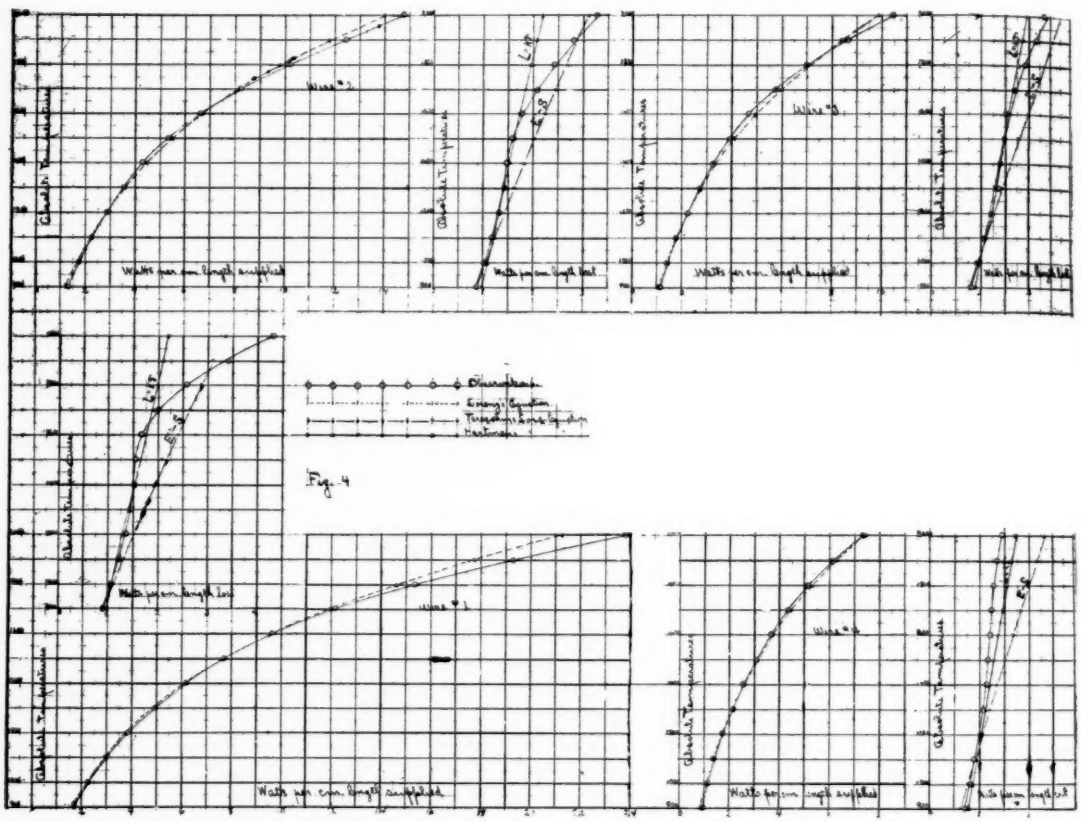


Fig. 4.

Fig. 4.

These results are all shown graphically in Fig. 4. It will be noted that the values of E' as computed from Lorenz's equation coincide with the observed curve of energy supplied to each wire with great exactness up to 1700 or 1800° Absolute, but that in the case of the convection and conduction loss curves the equation

$$L = kT$$

represents the loss actually observed much more closely than the values of $E' - T$ obtained by Tereschin's method.

By applying the method of least squares to the observed data for each wire for temperatures ranging between 1000°–1700° Absolute, as given in the second part of Table I., the values of A and B in Lorenz's equation can be obtained for each wire. With these values one can then compute the quantity of energy required to heat the given wire to any desired temperature. If one should plot the values of energy thus computed from Lorenz's equation, together with the observed values of energy supplied, as given in Table I., as ordinates and absolute temperatures as abscissæ, the curves thus obtained would apparently coincide with the corresponding curves of Fig. 4. Accordingly, the above-mentioned assumption of Tereschin receives the support of this additional evidence.

CERTAIN CASES OF THE VARIATION OF SOUND INTENSITY WITH DISTANCE.

BY G. W. STEWART.

IT is not possible to secure a source of sound without the presence of reflecting surfaces. In quantitative considerations one desires to know the variation of intensity with distance from the source and is thus led to inquire as to the deviations from the inverse square law caused by the reflectors. A case of practical interest is that in which a small vibrating area is located on a rigid sphere, for it is possible to construct a source which conforms very closely to these theoretical conditions.[1] An additional interest arises from the fact that an investigation of such a source leads to an estimate of the deviations from the inverse square law in the case of a person speaking or singing. Furthermore, by utilizing the results of the same theoretical investigation, we can obtain the relative intensities on a sphere when the distance of the sphere from a simple source is varied. These values give an estimate of the deviations from the inverse square law in the case of a person listening. The deviations in the case of a speaker are of interest in architectural acoustics: those occurring with the listener are of importance in the psychological laboratory.

With a small vibrating area located on a rigid sphere, the geometrical figure of the reflector makes a mathematical investigation possible. Lord Rayleigh[2] was the first to obtain an expression for the sound intensity in the various directions at a great distance from such a sphere. Subsequently the writer[3] extended the investigation in order to obtain similar results for distances that are not great.

A brief statement of the theory will doubtless prove helpful to the reader. Let the source be confined to a small area on the surface of the sphere within which $P_n(\mu)$ of Legendre's series approximates unity. Assume that the velocity of this area is represented by Ue^{ikat}, and that it has the same magnitude at all points. Assume that

ψ is the velocity potential,

a is the velocity of sound,

[1] Stewart and Stiles, PHYS. REV., N. S., Vol. I., No. 4, 1913, p. 309, and PHYS. REV., N. S., Vol. III., No. 4, 1914, p. 256.

[2] Rayleigh, Theory of Sound, Vol. II., p. 254.

[3] Stewart, PHYS. REV., XXXIII., No. 6, p. 467, December, 1911.

r is the distance from the center of the sphere,
c is the radius of the sphere,
dS is an element of surface of the sphere,
k is 2π/wave length,
γ is $k(at - r + c)$,

F is $\Sigma \frac{2n+1}{2} P_n(\mu) \frac{\alpha\alpha' + \beta\beta'}{\alpha^2 + \beta^2}$,

and that G is $\Sigma \frac{2n+1}{2} P_n(\mu) \frac{\alpha\beta' - \alpha'\beta}{\alpha^2 + \beta^2}$,

where $f_n^1(ikr) = \alpha' + i\beta'$
and $F_n^1(ikc) = \alpha + i\beta$.

Then $\psi = ka/2\pi r(F \sin \gamma + G \cos \gamma)\int\int Uds$. The mean potential energy, which is the "intensity" we desire, proves to be

$$\tfrac{1}{2}\rho_0 \frac{\dot{\psi}^2}{a^2} = \tfrac{1}{2}\rho_0(F^2 + G^2)\left(\frac{k}{2\pi r}\int\int UdS\right)^2.$$

In this formula $\left(\int\int UdS\right)^2$ measures the intensity of the source. For a constant source, a constant sound velocity and a fixed wave-length, the relative intensities are proportional to

$$\frac{(F^2 + G^2)}{r^2}. \qquad (1)$$

F and G are functions of k, r, c, and $\cos\theta$ or μ. The accompanying Fig. 1 will make clear the meaning of r, c and $\cos\theta$. The source is located at the point $(c, \theta = 0°)$. P is the point at which the intensity is desired and is located at a distance r and in the direction θ. Obviously P is any point on a circle whose radius is $r \sin\theta$ and whose circumference is everywhere at a distance r from the center of the sphere.

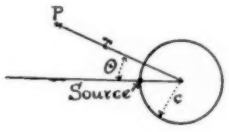


Fig. 1.

In view of (1), the deviations of the intensities from the inverse square law are indicated by relative values of $F^2 + G^2$. The computations involved in securing the numerical values of $F^2 + G^2$ are very laborious. Fortunately, certain numerical results are available, these having been obtained in previous investigations. As already indicated, the values of F and G depend upon those of ikr and ikc,[2] as well as upon μ.

[1] $f_n(ikr)$ and $F_n(ikc)$ are defined in Rayleigh's Theory of Sound, Vol. II., p. 238, and by Stewart, loc. cit.

[2] For the terms from which F and G can be computed in the two cases $kc = 0.5$, $kr = 25$ and $kc = 1.0$, $kr = 50$, see PHYS. REV., XXXIII., No. 6 (1911), Table I., p. 473, and Table II., p. 475.

Table I. indicates the variation in the relative values of $F^2 + G^2$ with r and with θ, the former being expressed in terms of c, the radius of the sphere. In order to show the percentage deviations in $F^2 + G^2$ which represent the percentage deviations from the inverse square law, the value of this sum is assumed to be unity at a distance of 50 c. Table I. utilizes the values of F and G when $k \times c$ is 1 and when $k \times r$ has the values 2, 3, 4 and 50. The values enclosed in parentheses are computed by substituting in each case for the distance r in (1) the distance from P the source on the sphere. In other words, the values in parentheses

TABLE I.

Relative Values of $(F^2 + G^2)$, *those at 50 c being assumed Unity.*

Radius of sphere, $c = \frac{\text{wave length}}{2\pi}$.

Distance.	$\theta = 0°$.	30°.	60°.	90°.	120°.	150°.	180°.
2 c	4.24 (1.10)	2.58 (.98)	1.14	.622	.396	.329	.270
3 c	2.26 (1.05)	1.81 (.98)	1.18	.728	.564	.446	.420
4 c	1.75 (1.03)	1.53 (.98)	1.15	.862	.661	.544	.520
50 c	1.00 (1.00)	1.00 (1.00)	1.00	1.00	1.00	1.00	1.00

indicate the deviations from the inverse square law when the distances are measured from the actual source rather than from the center of the sphere.

TABLE II.

Relative Values of $(F^2 + G^2)$, *Those of 200 c Being Assumed Unity.*

Radius of sphere $= 0.5 \times \frac{\text{wave-length}}{2\pi}$.

Distance.	$\theta = 0°$.	30°.	60°.	90°.	120°.	150°.	180°.
2 c	6.28 (1.59)	3.54 (1.30)	1.28	.652	.655	.765	.797
50 c	1.04 (1.01)	1.03 (1.01)	1.02	1.00	.978	.968	.957
200 c	1.00 (1.00)	1.00 (1.00)	1.00	1.00	1.00	1.00	1.00

Table II. contains the values obtained when $k \times c$ is 0.5 and when $k \times r$ has the values 1, 25 and 100.

The tabulated results show that when distances are measured from the center of the sphere the direction of minimum variation from the inverse square law is found to depend upon the wave-length. With the longer wave there is less deviation in the rear of the sphere and with the

For values of F and G for $kc = 1$ and $kr = 2, 3, 4$ and 50 see PHYS. REV., N. S., IV., No. 3, Table I., p. 255, and Table II. (60 cm.), p. 256.

The values of $F^2 + G^2$ for $kc = 0.5$ and $kr = 1.0$ and $kr = 100$ appear only in the form of curves, Fig. 2, PHYS. REV., XXXIII., No. 6, December, 1911.

shorter, less deviation in front. Both of these facts are in accord with anticipation based upon elementary considerations. If the distances in the directions 0° and 30° are measured from the source on the sphere there is less deviation from the inverse square law, but it is yet large. Whether distances be measured from the source or from the center of the sphere, the differences obtained by changing wave-length are very marked. This suggests that, in any practical case, a closer approximation to the inverse square law in front of the source can be secured by increasing the frequency of the tone. It also suggests the well-known fact that the relative intensities of the components of any sound will change with distance and direction from the source.

In order to utilize these numerical values for an estimate of the deviation from the inverse square law in the case of a speaker, it is necessary to assume that the head acts as a rigid sphere and that the source occupies but a small area on that sphere. If we choose as a circumference, 60 centimeters, the results in Table I. and Table II. refer to wave-lengths of 60 and 120 centimeters respectively. Although the lack of conformity to the theoretical conditions is obvious, yet we can consider that the above results furnish a fairly satisfactory estimate of the deviations from the inverse square law in the case of a speaker or singer using tones approximately 60 and 120 centimeters in wave-length, or approximately 575 and 287 in frequency. With the sphere circumference 60 centimeters, the distances are approximately 19.1, 28.6, 38.2 and 477 centimeters in Table I., and 19.1, 477 and 1,910 centimeters in Table II. In the former table, with a frequency 575, the deviations from the inverse square law at the above distances are over 400 per cent. If the distance to the source of sound instead of to the center of the head is substituted in the inverse square formula, then the deviations are 10 per cent. or less. The deviations in various directions are readily read in the tabulation. Table II. should be used for a frequency approximating 287. Neither table gives the relations between intensities at points having a constant r and varying values of θ, for such a comparison has already been published.[1]

In order to apply the results to the case of hearing, we must have recourse to the reciprocal theorem of Helmholtz,[2] which permits us to interchange positions of the source and the points at distances r where the relative intensities are desired. Then we can consider a simple source at a distance r from the center of the head (or, using the parenthetical results, from the ear) and can obtain an estimate of the variation of intensity with distance from either ear. For the frequency 575, the maximum deviation

[1] Stewart, PHYS. REV., XXXIII., No. 6, December, 1911.

[2] Rayleigh, Theory of Sound, Vol. II., p. 294.

from the inverse square law with distances from the center of the head to the source of approximately 19.1 and 477 centimeters (9.5 to 468 centimeters from the ear) does not exceed 10 per cent. (see Table I., 0°). For the frequency 287 and the same distance from the ear, the deviation is almost 60 per cent. (see Table II., 0°). If with the latter frequency distances of 477 to 1,910 centimeters are selected, the deviation is only 1 per cent. There is a distinct advantage in using the higher frequency in cases where an estimate of relative intensities is obtained by using the inverse square law.

PHYSICAL LABORATORY,
STATE UNIVERSITY OF IOWA.

DISTRIBUTION OF CURRENT BETWEEN A GAS COLUMN AND A METALLIC SHUNT.

BY ROBERT F. EARHART.

THESE experiments were made for the purpose of studying some of the conditions under which a current of electricity passing through a gas might be diverted through a metallic circuit. It was desired also to study the quantitative distribution between a gas column and a metallic circuit under several conditions.

An article by Lehman[1] deals with this topic in a qualitative way. Among other experiments Lehman sent a discharge produced by a static machine through a long tube across which perforated metallic diaphragms were placed. These could be connected externally. The changes in appearance of the luminous discharge which resulted when cross connections were made is described and these are illustrated by colored plates.

The general form of apparatus used in the present experiment consisted of a cylindrical glass tube closed at each end by a flat electrode. The tube was provided with pump connection. Within the tube perforated metallic partitions were placed parallel to the end electrodes. These partitions were provided with terminals sealed through the walls of the tube. They could be connected through a switch and low resistance galvanometer. A current from a high potential storage battery sent through the tube was measured either with a milliammeter or shunted galvanometer.

A considerable number of experiments were made with tubes of different size, under varying pressure conditions and for currents varying from a few microamperes to fifty milliamperes.

When a current flows through a metallic circuit terminated by diaphragms in the manner described, the diaphragms must continually acquire charges from the gas column. One of the first points to be investigated was the probable mechanism by means of which these partitions acquire charges. For this purpose several pairs of diaphragms were made in which the ratio between area of aperture and area of metal partition was kept constant. A pair containing a large number of small holes was found to be more effective in diverting current than a pair having a few larger openings. Moreover this effectiveness was

[1] Ann. der Phys., VII., p. 1, 1902.

increased by increasing the thickness of the metal walls. This indicated that the diaphragms acquire charge as the streams of ionized gas pass through the openings rather than by direct impingement of ions on the metal partition.

A fine meshed copper gauze is effective in diverting current from the gas column but two layers of gauze separated a few millimeters and with the edges connected is many times more effective. This indicates again that the terminals of the shunt circuit acquire charge by diffusion from the gas.

If the diaphragms are separated a distance commensurate with the length of the tube, the effect of closing the shunt circuit is to diminish the total current traversing the tube. Here offering an alternative path diminishes the total current. In fact when the gas pressure is low (1/20 mm.) closing the external circuit quenches the discharge entirely. It appears that the conducting gas is impoverished by diversion of some of the ions.

While the proportion of total current diverted through the shunt depends to a large extent on the terminal conditions of this circuit, certain characteristics are exhibited which are common to all of the cases studied. A typical case is represented in Fig. 1.

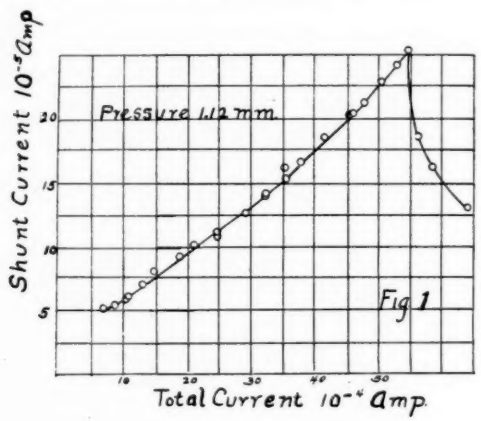


Fig. 1.

The discharge tube in this case was 52.8 mm. long and 14 mm. in diameter. The copper partitions were .4 mm. thick and were placed so as to divide the tube transversely into three equal compartments. Each partition had 16 apertures of 1 mm. diameter. Total area of aperture = .123 sq. cm. Total area metal partition = 1.415 sq. cm. If one notes the difference in value of ordinates and abscissae it will be observed that approximately 10 per cent. of the total current passes through the

shunt circuit for small values of the current and that this proportionality is constant with increase in current up to a limiting value, when further increase in total current is accompanied by decrease in shunt current.

Figs. 2 and 3 show members of a family of curves taken with the same tube under other pressure conditions. The slope of the lower portion of the curves indicates the same proportionality between shunt and total current for the small values of current. They indicate that the limiting

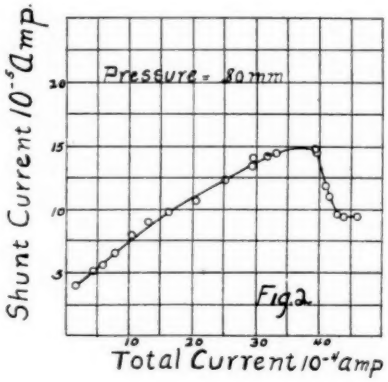


Fig. 2.

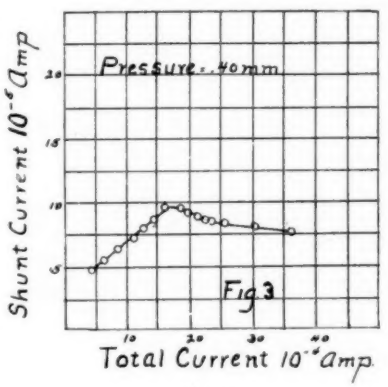


Fig. 3.

value is determined by the pressure. A similar experiment was made with this tube, one partition being of double thickness. When the thinner partition was opposite the anode the results gave rise to a family of curves precisely similar to the cases shown in Figs. 1, 2 and 3. With the thicker partition opposite the anode the same slope of curves were obtained for small values but larger currents could be sent through the tube before the limiting value was attained.

This lack of symmetry obtained upon reversal of the direction of current through the tube was studied in a rather extended series of measurements where in one diaphragm was altered in size, number of openings, and thickness while the configuration of the other was maintained constant. This group of experiments may be summarized by stating that a decided lack of symmetry exists upon interchanging anode and cathode and that the terminal collecting the positive charges from the gas places the limitation on the carrying capacity of the shunt circuit.

The experiments hitherto described were made with small currents. It was desired to alter the conditions so that measurements of current could be made directly with a milliammeter. A tube 3 cm. in diameter and 12 cm. long was provided with a pair of double gauze partitions arranged so as to divide the tube into three approximately equal sections. The battery used would produce a current of 50 milliamperes in the

tube when the air pressure was equal to .5 mm. of Hg. Starting with a small current, the entire current could be lead through the shunt, the space between the diaphragms being nonluminous. Currents up to 8 milliamperes could be thus diverted. A further small increase above 8 milliamperes produced an unstable condition, the shunt current varying from 2 to 8 milliamperes, the remainder flashing through the gas. Passing this unstable state the current through the shunt decreased to 2 m.a. and remained at that value while the total current was increased to 50 m.a. The values when plotted give rise to a curve possessing the same general features represented in Fig. 1.

SUMMARY.

1. The effectiveness of electrodes in taking current out of a conducting gas column depends more upon the state of division of the electrodes than upon their superficial area.

2. The effect of offering an alternative path through an external metallic conductor is to decrease the total current.

3. For small currents an increase through the shunt circuit occurs when the total current increases. Such increases are proportional to the total current but the value of the factor depends on the pressure of the gas and form of the electrodes.

4. The proportionality factor referred to in (3) holds up to a limiting value which depends on the pressure employed. Further increase in total current results in a decrease in current through the shunt circuit.

PHYSICAL LABORATORY,
OHIO STATE UNIVERSITY,
December, 1915.

SELECTIVE RADIATION FROM OSMIUM FILAMENTS.

BY ERNEST F. BARKER.

I. INTRODUCTION.

THE problem of selective radiation from metals is of especial interest in connection with the study of incandescent lamps because of its direct bearing upon the question of luminous efficiency. If all incandescent sources exhibited the properties of a black body it is clear that luminous efficiency would be a function of temperature only, and any choice between materials for high efficiency illumination would be upon the basis of their relative abilities to withstand high temperatures. Experiment shows, however, that this is not the case. In many, if not all radiators the emissivity is found to vary with the wave-length, the energy curve for pure metals being generally somewhat depressed in the region of longer wave-lengths. The ratio of luminous to total energy radiated is therefore higher than for a black body. The existence of a general effect of this type was anticipated some time ago by Aschkinass[1] in the approximate displacement law for metals

$$\lambda_M T = 2{,}666,$$

derived from Maxwell's equations, in which the constant, and hence the value of λ_M, is lower than for the black body. It has also been shown experimentally for many different filaments, but its magnitude is not readily measurable owing to the lack of a satisfactory method for determining operating temperatures. In 1910 Hyde[2] published a table showing the relative efficiencies of various filaments when operated, not at the same temperature, but at a "color match" with a given standard lamp. This probably arranges them in the proper order, since if there were no selectivity a color match would mean the same temperature of operation. It throws no light, however, upon the question of a possible temperature variation.

If the emissivity E is independent of temperature and the Wien equation is assumed for black body distribution, it should be possible to represent the spectral energy curve of any metallic radiator by the equation

[1] Aschkinass, Ann. d. Phys., 17, p. 960, 1905.
[2] Hyde, Jour. Franklin Inst., 170, p. 32, 1910.

$$J = \frac{c_1 E_\lambda}{\lambda^5 e^{\frac{c_2}{\lambda T}}}. \qquad (1)$$

Attempts to fit this relation to experimental data for various spectral energy curves, assuming E to be some simple function of λ, as, for example, $E = k\lambda^a$, have, however, not been entirely successful.[1] Whether the difficulty lies in the choice of the function E_λ, or in a variation of selectivity with temperature, remains to be determined, but Hyde[2] has demonstrated by means of a simple criterion obtained directly from equation (1) that such variations probably do exist in the case of tungsten filaments. Bidwell[3] has found evidence of a similar effect by direct measurements upon a mass of nickel whose temperature could be observed and controlled over a considerable range.

One of the objects of the present investigation is to determine whether or not the osmium filament exhibits a temperature variation of selectivity. Osmium was chosen for study in this connection because, in the first place, its selectivity is probably higher than that of most other metals so that the effects sought will be most easily measurable, and secondly, its characteristics have not been very fully described so that any data obtained from it will be of interest. The lamps, which were obtained through the courtesy of Dr. Hyde, of the Nela Research Laboratory, consume normally about 39 watts at 42 volts, giving approximately .55 candle power per watt. The filaments consist of two separate loops in series, each anchored to the glass bulb at the outer end. The investigation consists of (1) a study of the behavior of three osmium lamps under various operating conditions, with a test for selectivity; (2) a qualitative study, by comparison with carbon lamps, of the characteristic radiation from these filaments, showing variations of emissivity with temperature, and indicating the shape of the energy curve for at least a part of the visible spectrum; (3) a similar investigation of the near infra-red region of the spectrum.

II. Experimental Results in the Visible Spectrum.

1. *Lamp Characteristics.*

As a preliminary study the three osmium lamps were compared with each other and with an untreated carbon lamp for current and power consumption, candle power, and color at various voltages. The photometer measurements were against a secondary standard which was

[1] Coblentz, Bull. U. S. Bureau of Standards, 5, p. 339, 1909.

[2] Hyde, Astrophysical Jour., 36, p. 131, 1912.

[3] Bidwell, Phys. Rev., 3, p. 439, 1914.

several times carefully compared with a lamp furnished by the Bureau of Standards. This lamp had been calibrated at each of eight different voltages, thus making it possible to almost completely eliminate errors due to color differences. All measurements were by the method of

TABLE I.

Osmium Lamp No. 1.

Volts.	Amperes.	Watts.	Candle Power.	Watts per Candle.
5	.242	1.21		
10	.377	3.77		
13	.441	5.74		
16	.503	8.05		
20	.580	11.60	.91	12.74
23	.637	14.65	1.70	8.62
26	.683	17.76	2.99	5.92
30	.755	22.65	5.55	4.09
33	.800	26.40	8.20	3.22
36	.847	30.52	11.69	2.61
40	.908	36.32	18.00	2.02
42	.938	39.40	21.48	1.835
Normal values. 40.25	.910	36.63	18.30	2.00

substitution, but they represent candle power only in a single direction, since the osmium filaments at incandescence soften sufficiently to preclude the possibility of rotating them. The three lamps were not found to differ materially, and the data for filament No. 1 appears in Table I. and Fig. 1.

It would seem of interest to represent these relations for all the lamps by single algebraic functions, if possible. Middlekauff and Skogland[6] have shown that the variations of amperes, watts, candle power and watts per candle power with impressed voltage, for tungsten lamps of any type, may be expressed by an equation of the form,

$$y = Ax^2 + Bx + C,$$

where x is the logarithm of the ratio of any voltage to a chosen normal voltage, and y is the logarithm of the corresponding ampere, watt or candle power ratio, or the logarithm of the actual watts per candle. The value of C is, then, the logarithm of the normal watts per candle for the last equation, and zero for the first three, since they each represent curves passing through the origin.

Following this suggestion, equations of the same form were tried for

[6] Middlekauff and Skogland, PHYS. REV., 3, p. 485, 1914.

osmium lamps for the volts-watts and volts-candle-power variations. It is easily seen that if such a relation holds for the two cases $y_1 = \log w/w_0$ (log. watt ratio) and $y_2 = \log c/c_0$ (log. candle power ratio), it necessarily

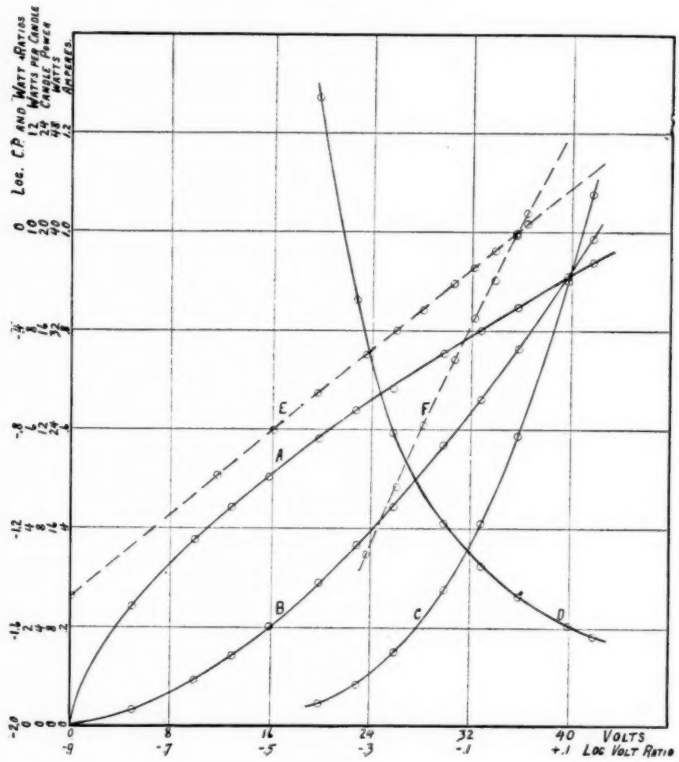


Fig. 1.

Characteristic Curves for Osmium Lamp No. 1. *A*, amperes; *B*, watts; *C*, candle power; *D*, watts per candle; *E*, log. watt ratio; *F*, log. candle power ratio.

holds for $y_3 = \log a/a_0$ (log. ampere ratio) and for $y_4 = \log w/c$ (log. watts per candle), for

$$\frac{w}{w_0} = \frac{a}{a_0} \cdot \frac{v}{v_0},$$

$$\log \frac{w}{w_0} = \log \frac{a}{a_0} + \log \frac{v}{v_0},$$

or

$$y_1 = y_3 + x.$$

But if

$$y_1 = Ax^2 + Bx,$$

then

$$y_3 = Ax^2 + (B - 1)x,$$

a function of the same form. Similarly, taking the logarithm of

$$\frac{w}{w_0} \div \frac{c}{c_0} = \frac{w}{c} \div \frac{w_0}{c_0},$$

we have

$$y_1 - y_2 = y_4 - (y_4)_0,$$

or

$$y_4 = y_1 - y_2 + (y_4)_0$$
$$= (A_1 - A_2)x^2 + (B_2 - B_1)x + C.$$

The normal consumption chosen was 2 watts per candle power, and the corresponding normal values of watts and candle power as they appear in Table I., were taken from the curves. The coefficients were determined by the method of least squares from the data taken upon filament no. 1, and the resulting equations are as follows:

(A) $$y_1 = 0.026609x^2 - 1.65072x$$

where x = log volt ratio, and y_1 = log watt ratio, and

(B) $$y_2 = -1.24490x^2 - 3.91898x$$

where x = log volt ratio, and y_2 = log c.p. ratio.

Table II. shows how nearly these equations represent the desired relations. It is to be noticed that the percentage of error to be expected in the candle power determinations is comparatively large because of the faint illumination at lower voltages.

The three available osmium lamps are all of the same type, so it is not possible to show that these equations are of general applicability. However, having been derived from the data for filament no. 1 only, they were found to apply almost as well to filaments no. 2 and no. 3 when the proper normal values were inserted.

TABLE II.

(A) Volts-Watts Relation for Filament No. 1.

Volts.	y_1 = Log (Watts ÷ 36.63)		Watt Ratio.		Per Cent. Difference.
	Computed.	Observed.	Computed.	Observed.	
10	−.98857	−.98750	.1027	.1029	+.20
13	−.80380	−.80493	.1978	.1973	−.25
16	−.65708	−.65804	.2203	.2198	−.23
20	−.49894	−.49938	.3170	.3167	−.09
23	−.39962	−.39800	.3985	.3990	+.13
26	−.31235	−.31440	.4871	.4849	−.45
30	−.21028	−.20877	.6162	.6183	+.34
33	−.14219	−.14224	.7208	.7207	−.01
36	−.07995	−.07926	.8512	.8526	+.16
40	−.00447	−.00369	.9898	.9915	+.17
42	+.03051	+.03166	1.0728	1.0756	−.28

(*B*) *Volts-Candle-Power.*

Volts.	y_2 = Log (C.P. + 18.30)		Candle Power Ratio.		Per Cent. Difference.
	Computed.	Observed.	Computed.	Observed.	
20	−1.30518	−1.30341	.0495	.0497	− .40
23	−1.02600	−1.03200	.0942	.0929	+1.40
26	− .78867	− .78678	.1627	.1634	− .43
30	− .52055	− .51816	.3016	.3033	− .56
33	− .34731	− .34864	.4495	.4481	+ .31
36	− .19290	− .19464	.6563	.6537	+ .40
40	− .01063	− .00718	.9758	.9836	− .80
42	+ .07199	+ .06958	1.1803	1.1815	− .10

The curves corresponding to (A) and (B) are plotted with a broken line upon Fig. 1. It will be noted that (A) represents very nearly a straight line. Assuming it to be actually straight, with a slope of $m = 1.65$, the relation could be written in the form

$$W = c_1 V^m,$$

where W = watts radiated and V = volts. Now if

$$W = IV = \frac{V^2}{R}$$

be substituted, where R is the resistance, this becomes

$$W = c_2 R^{\frac{m}{2-m}} = c_2 R^{\beta},$$

and if the resistance be proportional to absolute temperature, as it is very nearly for tungsten at high temperatures,[7]

$$W = c_3 T^{\beta} = c_3 T^{4.71}.$$

The value of this exponent, even though only a rough approximation, is of interest. For a black body its value is 4, and Hyde[8] has found experimentally $\beta = 4.7$ for tantalum and $\beta = 6.0$ for tungsten.

Direct evidence of the selectivity of the osmium filaments is obtained by comparing the watts per candle power which they radiate with the watts per candle power radiated by a carbon lamp when the two are at a color match, *i. e.*, when the ordinates of the spectral energy curves are proportional throughout the visible spectrum. Under these conditions, if there were no selectivity, both would be at the same temperature and both would have the same luminous efficiency. As appears from Table III., however, the osmium filament is much more efficient than the carbon, indicating that when the energy distribution is the same for

[7] Pirani, Phys. Zeitsch., 13, p. 753, 1912.

[8] *Loc. cit.*

both in the visible part of the spectrum, the curve for the osmium must lie considerably below that of the carbon at longer wave-lengths. This relation will be discussed further in connection with the study of the infra-red radiation.

TABLE III.

Carbon and Osmium Filaments at Color Match.

Carbon No. 1.		Osmium No. 1.		Ratio Watts per Candle.
Volts.	Watts per Candle.	Volts.	Watts per Candle.	
180	9.35	26.0	5.92	.633
190	7.15	28.3	4.75	.665
200	5.61	30.8	3.81	.679
210	4.51	33.3	3.15	.697
220	3.72	35.8	2.65	.713

2. Variations of Emissivity with Temperature.

Under the caption of "Criterion I" Hyde[9] has described a comparatively simple method for investigating qualitatively the temperature variations in emissivity from any source, as follows: Equation (1) may be considered as defining emissivity E, which we will assume to be independent of temperature.

[9] *Loc. cit.*

$$J = \frac{c_1 E}{\lambda^5 e^{\frac{c_2}{\lambda T}}}. \tag{1}$$

Suppose a black body B, and any other substance A having an emissive power E and radiating in accordance with this equation, are at such temperatures that for a chosen pair of wave-lengths each has the same relative intensities, *i. e.*,

$$\left[\frac{J_{\lambda_1}}{J_{\lambda_2}}\right]_A = \left[\frac{J_{\lambda_1}}{J_{\lambda_2}}\right]_B. \tag{2}$$

Let the temperature of B be increased by a given small amount, and the temperature of A by such an amount that the same condition again holds, and

$$\left[\frac{J_{\lambda_1} + dJ_{\lambda_1}}{J_{\lambda_2} + dJ_{\lambda_2}}\right]_A = \left[\frac{J_{\lambda_1} + dJ_{\lambda_1}}{J_{\lambda_2} + dJ_{\lambda_2}}\right]_B. \tag{3}$$

Differentiating (1) and combining with (2) and (3) we obtain

$$\left[\frac{dJ_{\lambda_1}}{J_{\lambda_1}}\right]_A = \left[\frac{dJ_{\lambda_1}}{J_{\lambda_1}}\right]_B \quad \text{and} \quad \left[\frac{dJ_{\lambda_2}}{J_{\lambda_2}}\right]_A = \left[\frac{dJ_{\lambda_2}}{J_{\lambda_2}}\right]_B,$$

i. e., for either wave-length the relative change of intensity due to the increase in T is the same for A as for the black body B. This may be written

$$\left[\frac{J_{\lambda_1} + dJ_{\lambda_1}}{J_{\lambda_1}}\right]_A = \left[\frac{J_{\lambda_1} + dJ_{\lambda_1}}{J_{\lambda_1}}\right]_B \qquad (4)$$

with a similar relation holding for wave-length λ_2. Equations (2), (3) and (4) constitute criterion I., (4) following from (2) and (3) necessarily if (1) properly represents the energy distribution in the spectrum of A, *i. e.*, if the emissivity is independent of the temperature. Equation (4) is a necessary, though not a sufficient condition for this constancy of E with respect to T. Hence if the radiation from any substance does not obey criterion I., its emissivity is a function of temperature. The application of criterion I. may be made directly with a spectrophotometer by measuring the various intensities at two wave-lengths for the radiators which are to be compared.

If, for given temperatures of A and B, equation (2) holds, not simply for two particular wave-lengths, but for any arbitrarily chosen pair of wave-lengths in the visible spectrum, then each source radiates the same proportionate amount of energy for each spectral region. Equation (2) is thus the condition for what may be called an integral color match. With a Lummer-Brodhun contrast photometer it is possible to adjust two sources quite accurately for such a color match, and this affords a satisfactory and somewhat less laborious method of applying criterion I., by measuring the relative variations in total intensity.

Data are here presented for the comparison of the osmium filaments with two untreated carbon filaments. The latter, though not black bodies in the strict sense, form very convenient reference standards, and are sufficiently non-selective to be quite acceptable. Direct measurements against a standard electrically heated black body are, in fact, very difficult owing to the impossibility of obtaining temperatures comparable with those of the incandescent filament, and also because the highest temperatures available can scarcely be kept constant while the comparison is being made. Criterion I. has been tested, both with the photometer and with the spectrophotometer, using a range of temperatures for the carbon lamps corresponding to impressed voltages from 180 to 220. In every case it has been shown that there is actually a change of emissivity with temperature.

Photometric Data.—A Lummer-Brodhun contrast photometer of the ordinary type was used, with an adjustable bench about seven meters in length. The two sources to be compared were carefully screened, and two diaphragms with apertures about ten by fifteen centimeters were mounted between the photometer and each lamp. All light not coming directly from the lamps was excluded as completely as possible, and in

order to eliminate any effects due to construction and arrangement of the system, a part of the observations were taken with the reference standard at each end of the bench. The three test lamps were each carefully color matched against both carbon filaments at voltages for the latter ranging from 220 to 180 volts in ten volt intervals, the corre-

TABLE IV.

Voltages and Relative Intensities for Integral Color Match.

A, Mean color match voltage of test lamp. *B*, Mean relative intensities of test lamp and comparison lamp. *C*, Ratio of relative intensities in terms of values corresponding to normal voltage of comparison lamp.

Series I. Photometer length 400 cm. Comparison lamp carbon No. 2.

Test Lamp.		Comparison Lamp Voltages.				
		180	190	200	210	220
Osmium no. 1.....	A	26.0	28.6	30.9	33.1	35.8
	B	.837	.837	.824	.781	.776
	C	1.08	1.08	1.06	1.01	1.00
Osmium no. 2.....	A	26.0	28.4	30.8	33.6	36.2
	B	.817	.815	.800	.794	.779
	C	1.05	1.05	1.03	1.02	1.00
Osmium no. 3.....	A	26.1	28.7	31.4	33.5	36.2
	B	.851	.826	.837	.791	.783
	C	1.09	1.05	1.07	1.01	1.00

Series II. Photometer length 500 cm. Comparison lamp carbon No. 1.

Osmium no. 1.....	A	26.0	28.3	30.8	33.3	35.8
	B	.798	.767	.755	.743	.733
	C	1.09	1.05	1.03	1.01	1.00
Osmium no. 2.....	A	26.5	28.8	31.3	33.9	36.3
	B	.819	.789	.788	.783	.764
	C	1.07	1.03	1.03	1.02	1.00
Osmium no. 3.....	A	26.6	28.7	30.9	33.4	36.1
	B	.851	.814	.772	.755	.753
	C	1.13	1.08	1.03	1.00	1.00

Series III. Photometer length 500 cm. Comparison lamp tantalum No. 1.

		70	80	90	100	110
Osmium no. 1.....	A	32.1	36.8	41.3	45.7	49.8
	B	1.619	1.530	1.480	1.405	1.358
	C	1.19	1.13	1.09	1.03	1.00

sponding relative intensities being recorded (Table IV., *B*). *Criterion I. is fulfilled if these relative intensities are constant for each set of observations,*

as follows from equation (4), or, in other words, if the ratio of the relative intensities corresponding to two different temperatures (Table IV., *C*) is unity. Since the carbon lamps cannot be operated at a temperature sufficiently high to match in color the osmium filaments near their normal temperature, a comparison was also made between osmium filament no. 1 and a tantalum lamp, tantalum having been found to very nearly fulfill criterion I.[1] This appears in the table as Series III.

Considerable difficulty was encountered at the lower temperatures in making the color match because of the faint illumination, so that the first series of readings was taken with the photometer bench at 400 cm. Series II., with a length of 500 cm., is probably more accurate for the higher voltages, but less accurate for the lower, as appears from the variations in *C*, Table IV. While the results are not quite as consistent as might be desired, they show without exception that *there is a considerable departure from the conditions upon which criterion I. depends.*

It must be understood that there is a certain assumption underlying these conclusions, viz., that when a color match is obtained as above the ordinates of one spectral energy curve are actually proportional to the corresponding ordinates of the other curve, not simply in the brighter portion, but throughout the visible spectrum. This is the condition represented by equations (2) and (3), which must be satisfied before equation (4) is to be applied. Further investigation with a spectrophotometer, therefore, seemed desirable.

Spectrophotometric Data.—The instrument used was of the Lummer-Brodhun type, manufactured by Schmidt and Haensch, and was equipped with a variable sectored disc as designed by Hyde, giving a continuous range of transmissions from about 60 per cent. down to 0 per cent. This was calibrated in position by comparison with several standard discs. The slit width used on each collimator was .4 mm., and before each slit diffusing screens of ground glass were mounted. The method of substitution was employed throughout, two lamps being compared by successive balancing against a fixed comparison source, and the latter frequently tested for changes in temperature and color by comparison with a standard. During the course of some months the variation of the comparison source was almost imperceptible. Under these conditions no slit width corrections are necessary for the relations expressed by equations (2), (3) and (4), so long as the width of the collimator and ocular slits is not changed, because the correction factor, depending only upon the wave-lengths and the shape of the energy curve under investigation, cancels out in each case. The conclusions to be deduced are, therefore, quite independent of the purity of the spectra compared.

[1] Hyde, *loc. cit.*

The preliminary observations involved a comparison of the spectral energy curves for osmium and carbon at various color match temperatures, through as wide a range of wave-lengths as possible. No marked differences between them were noted, the agreement being sufficiently close to indicate that no particular region of the spectrum demands special attention. Hence the conclusion seemed justified that if the curves are matched at four or five wave-lengths about equally spaced across the visible region, they will show satisfactory agreement throughout. As a matter of fact, however, there was some tendency, scarcely greater than the necessary experimental error, toward larger ratios in the middle region of the spectrum, indicating an elevation of the osmium curve with respect to the carbon, and later observations show the same effect. This conclusion is not in agreement with a statement published by Hyde,[1] for he found "slight evidence in the case of osmium that the curve of the latter when showing the same relative distribution between the energy emitted at 0.7 μ and that emitted at 0.5 μ as compared with carbon, dropped a little below that of the carbon at intermediate wave-lengths." These variations are not, however, of sufficient magnitude to noticeably affect the results here presented.

Test for Variations of Emissivity with Temperature.—In order to avoid the tedious process of spectrophotometric color matching by repeated trials with slightly varying voltages in each of the temperature regions

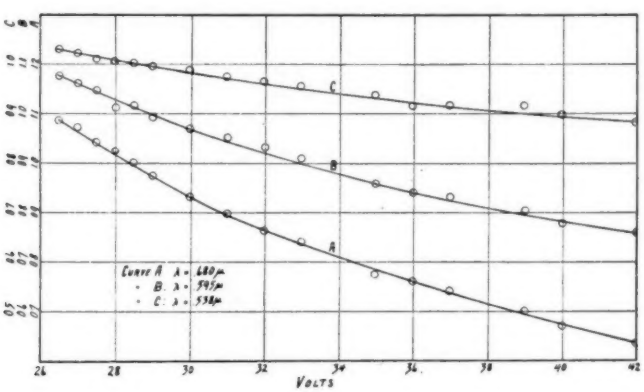


Fig. 2.
Color Ratios for Osmium No. 1.

to be studied, the following method was adopted. Measurements upon each lamp of the intensities for wave-lengths .680 μ, .595 μ, .538 μ and .500 μ in terms of the corresponding intensities of the comparison source

[1] Hyde, Jour. Franklin Inst., 170, p. 31, 1910.

were taken for a number of different voltages at arbitrary intervals. A set of ratios, which will be referred to as "color ratios," were then computed and plotted. These represent the quotient of the intensity for the shortest observed wave-length, $\lambda = .500\,\mu$, by the intensities at the same temperature for the other three wave-lengths. The three numbers so obtained may be used as an index of the color of the test

TABLE V.

Lamp.	Voltage.	Color Ratios.				Observed Transmission.			
		$\lambda = .680\mu$	$.595\mu$	$.538\mu$	$.500\mu$	$.680\mu$	$.595\mu$	$.538\mu$	$.500\mu$
O no. 1	35.97	.759	.844	.925	1.00	.1839	.1658	.1520	.1396
O no. 2	36.12	.759	.843	.917	1.00	.1597	.1437	.1320	.1211
O no. 3	35.70	.759	.849	.925	1.00	.1610	.1431	.1325	.1227
	mean	.759	.845	.922	1.00				
C no. 1	220.2	.759	.850	.925	1.00	.1000	.0906	.0831	.0761
C no. 2	222.2	.759	.846	.925	1.00	.1216	.1090	.0991	.0910
	mean	.759	.848	.925	1.00				
O no. 1	33.50	.820	.891	.946	1.00	.2404	.2210	.2086	.1985
O no. 2	33.45	.820	.888	.938	1.00	.2105	.1960	.1852	.1743
O no. 3	33.35	.820	.895	.950	1.00	.2074	.1888	.1775	.1690
	mean	.820	.891	.945	1.00				
C no. 1	210.0	.820	.890	.937	1.00	.1309	.1214	.1145	.1091
C no. 2	212.8	.820	.886	.941	1.00	.1580	.1458	.1380	.1303
	mean	.820	.888	.939	1.00				
O no. 1	31.00	.895	.947	.971	1.00	.3234	.3042	.2974	.2900
O no. 2	30.90	.895	.946	.965	1.00	.2850	.2700	.2650	.2555
O no. 3	31.00	.895	.945	.975	1.00	.2707	.2553	.2491	.2422
	mean	.895	.946	.970	1.00				
C no. 1	200.0	.895	.940	.960	1.00	.1774	.1684	.1634	.1579
C no. 2	202.4	.895	.936	.965	1.00	.2150	.2055	.1990	.1926
	mean	.895	.938	.962	1.00				
O no. 1	28.93	.978	.996	.995	1.00	.4160	.4080	.4088	.4060
O no. 2	28.78	.978	1.002	.992	1.00	.3750	.3675	.3667	.3650
O no. 3	28.76	.978	1.000	.998	1.00	.3597	.3504	.3535	.3520
	mean	.978	.999	.995	1.00				
C no. 1	190.0	.978	1.002	.994	1.00	.2459	.2341	.2404	.2409
C no. 2	191.6	.978	.991	.990	1.00	.3075	.3045	.3032	.3015
	mean	.978	.997	.992	1.00				
O no. 1	26.75	1.075	1.069	1.028	1.00	.5500	.5555	.5785	.5947
O no. 2	26.50	1.075	1.067	1.024	1.00	.5040	.5040	.5325	.5425
O no. 3	26.50	1.075	1.066	1.024	1.00	.4900	.4935	.5087	.5225
	mean	1.075	1.067	1.025	1.00				
C no. 1	180.0	1.075	1.073	1.016	1.00	.3497	.3538	.3706	.3744
C no. 2	182.4	1.075	1.058	1.017	1.00	.4200	.4278	.4428	.4527
	mean	1.075	1.065	1.016	1.00				

lamp, since two lamps will match in color only when these ratios are the same for each. Fig. 2 shows the variations in color ratios for osmium filament no. 1, and makes it possible to find the voltage corresponding to any desired color.

The voltage of each lamp when at color match with carbon no. 1 at 180, 190, 200, 210 and 220 volts may be read from these curves immediately, and the exactness of the color match determined by the agreement of the corresponding color ratios. The figures appear in Table V. The average ratios for carbon and for osmium at each temperature show that a very nearly perfect match has been obtained, the differences between corresponding values for different filaments being not much greater than those for two similar filaments. The osmium ratios for yellow and green (.595 μ and .538 μ) seem to run slightly higher than those for carbon,

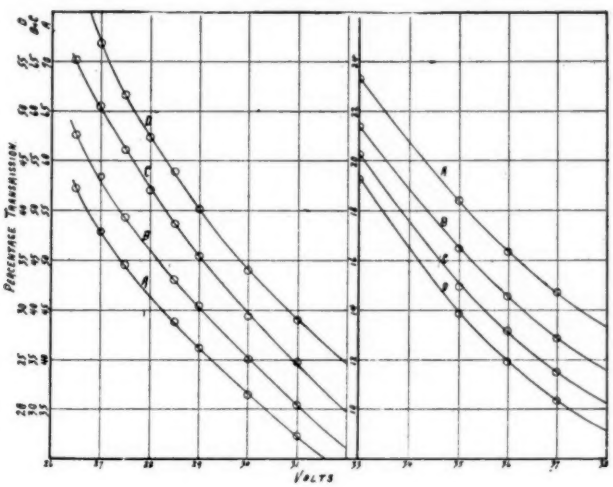


Fig. 3.

Isochromatic Curves for Osmium No. 1. Curve *A*, .680 μ; Curve B, .595 μ; Curve C, .538 μ; Curve D, .500 μ.

which agrees with the previous conclusion regarding the relative shapes of the curves. The agreement of these pairs of ratios constitutes the fulfillment of equation (3).

The same observations from which the above color ratios were computed may also be plotted in the form of isochromatic transmission-voltage curves, as in Fig. 3, the disc transmissions varying inversely as the intensities relative to the comparison source. From Fig. 3 we may determine the intensities for each of the four wave-lengths considered, at such voltages for osmium no. 1 (found from Fig. 2) as correspond to a color match with carbon no. 1 at the chosen voltages. These intensities,

the reciprocals of the disc transmissions appearing in Table V., *are precisely the data necessary for the application of criterion I.*

TABLE VI.

Intensity Ratios for Each Lamp when at a Color Match with Carbon Lamp No. 1.

$I_{\nu_1}/I_{\nu_2} = T_{\nu_2}/T_{\nu_1}$, I = intensity of emission, $\nu_1 < \nu_2$.
T = fractional transmission of disc.

Lamp.	Color Match Voltages.		Wave-lengths.			
			.680μ	.595μ	.538μ	.500μ
A. Color match with carbon No. 1 at 180 and 220 volts.						
O no. 1	26.75	35.97	.334	.298	.263	.235
O no. 2	26.50	36.12	.317	.285	.248	.223
O no. 3	26.50	35.70	.328	.290	.260	.234
		mean	.326	.291	.257	.231
C no. 1	180.0	220.0	.286	.256	.224	.203
C no. 2	182.4	222.2	.289	.255	.224	.201
		mean	.287	.255	.224	.202
B. Color match with carbon No. 1 at 190 and 220 volts.						
O no. 1	28.93	35.97	.441	.406	.372	.343
O no. 2	28.78	36.12	.425	.391	.360	.332
O no. 3	28.76	35.70	.447	.409	.375	.348
		mean	.438	.402	.369	.341
C no. 1	190.0	220.0	.407	.387	.346	.316
C no. 2	191.6	222.2	.395	.358	.327	.302
		mean	.401	.372	.336	.309
C. Color match with carbon No. 1 at 180 and 210 volts.						
O no. 1	26.75	33.50	.436	.397	.361	.332
O no. 2	26.50	33.45	.419	.390	.348	.321
O no. 3	26.50	33.35	.424	.382	.349	.324
		mean	.426	.390	.353	.326
C no. 1	180.0	210.0	.374	.344	.309	.291
C no. 2	182.4	212.8	.376	.340	.312	.288
		mean	.375	.342	.310	.289

The ratio of two intensities, or the inverse ratio of two transmissions, at any wave-length and a chosen pair of voltages for a given lamp, forms one member of equation (4). The other member is a similar intensity ratio for the other lamp at color match voltages and the same wave-length. These ratios for each lamp for various wave-lengths and various pairs of voltages appear in Table VI.; to satisfy equation (4) the values for the osmium lamps at any wave-length should equal those for the

carbon lamps at the same wave-length, in any one of the three groups. The mean values show a very wide deviation from equality, however, and always in the same direction. *Hence criterion I. is not fulfilled*, and there is a change of emissivity with temperature, even at the short wave-lengths within the visible spectrum.

III. Comparison of the Infra-red Spectra of Carbon and Osmium.

The marked depression of the energy curve of osmium with respect to that of carbon filaments in the longer wave-lengths suggests at once the application of criterion I. in the infra-red. This has been done, using a fixed arm mirror spectrometer with a quartz prism, set up accord-

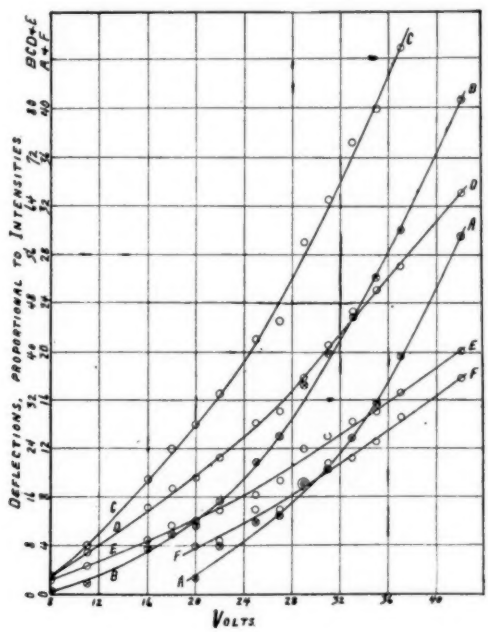


Fig. 4.

Isochromatic Curves for Osmium No. 1. Curve *A*, .608 μ; Curve *B*, .726 μ; Curve *C*, 1.068 μ; Curve *D*, 1.750 μ; Curve *E*, 2.098 μ; Curve *F*, 2.400 μ.

ing to Wadsworth's[1] method for minimum deviation. The Cornu quartz prism, with faces 74 × 110 mm., was supplied by A. Hilger, Ltd., and its indices of refraction for various wave-lengths were determined from measurements by Paschen[2] upon a similar prism. The detector was a sensitive thermopile constructed by Coblentz, with a Leeds and Northrup high sensitivity galvanometer. With the scale at 128 cm. it

[1] Wadsworth, Phil. Mag., 38, p. 337, 1894.

[2] Paschen, Ann. d. Phys., 35, p. 1005, 1911.

gave a deflection of 80 mm. for a standard candle at one meter. The thermopile slit was .38 mm. in width, and so placed that it received an average spectral range of about 185 Ångstrom units.

The data consists of observations of the energy distributions at various temperatures for osmium lamp no. 1 and carbon lamp no. 1, from the extreme red of the visible spectrum to the longest wave-lengths giving appreciable deflections. The results for repeated trials were quite consistent, and are shown graphically for osmium no. 1 in Fig. 4. From such curves the mean galvanometer deflections of Table VII. were obtained. This table also shows the ratios of the intensities at various wave-lengths to those at $\lambda = 2.098\,\mu$ for each different temperature, which correspond to the color ratios for the visible spectrum. The intensity ratios are plotted in Fig. 5.

TABLE VII.

Galvanometer Deflections, and Intensity Ratios.

Deflections at Wave-lengths.						Volts.	$I_{2.098\mu} \div I_\lambda$					
λ=.608 μ	.726 μ	1.068 μ	1.750 μ	2.098 μ	2.400 μ		.608μ	.726μ	1.068μ	1.750μ	2.098 μ	2.400 μ
Osmium No. 1.												
	.6	3.1	3.0	2.3		8		3.83	.742	.766	1.00	
	3.3	10.7	8.2	5.6		12		1.70	.521	.683	1.00	
	7.1	19.0	13.7	9.0		16		1.27	.474	.656	1.00	
1.4	12.1	27.8	19.6	12.7	3.5	20	9.08	1.05	.457	.649	1.00	3.63
4.3	19.3	38.4	26.1	16.5	5.8	24	3.79	.855	.430	.632	1.00	2.84
7.6	29.2	52.0	33.5	21.2	8.2	28	2.79	.726	.408	.633	1.00	2.58
11.5	41.9	68.0	42.4	26.3	10.7	32	2.29	.629	.387	.621	1.00	2.46
17.4	56.5	85.5	51.8	31.6	13.3	36	1.82	.560	.370	.610	1.00	2.38
25.0	72.6	104.8	61.2	37.2	16.2	40	1.49	.512	.355	.608	1.00	2.30
29.5	81.5	114.5	66.0	40.2	17.8	42	1.36	.494	.351	.610	1.00	2.26
Carbon No. 1.												
12.2	51.0	145.5	109.0	76.3	31.3	180	6.25	1.50	.525	.700	1.00	2.43
14.2	63.6	168.5	122.8	84.7	34.1	190	5.96	1.33	.503	.690	1.00	2.48
18.3	78.2	191.5	136.5	93.0	36.8	200	5.09	1.19	.485	.681	1.00	2.53
23.1	96.2	214.4	150.5	101.3	39.6	210	4.39	1.05	.473	.674	1.00	2.56
29.7	119.0	240.0	166.0	109.6	42.4	220	3.68	.935	.456	.660	1.00	2.58

The variation of any intensity ratio with increasing voltage is an indication of the rate of increase of intensity with temperature for the given wave-length, relative to that for $\lambda = 2.098\,\mu$. Thus, in the case of the carbon lamp, the ratios for each wave-length shorter than $2.098\,\mu$ decrease (Table VII.), showing that the corresponding I_λ increases

more rapidly than does $I_{\lambda=2.098\mu}$, and the rate of decrease becomes more rapid with shortening wave-lengths. For $\lambda = 2.400\ \mu$ the ratios increase, showing that here I_λ increases more slowly than at $2.098\ \mu$. This is exactly as would be expected for black body radiation, according to Wien's displacement law. In the case of osmium, I_λ increases more rapidly for each shorter wave-length than for $2.098\ \mu$, but the last column shows a more rapid increase for $2.400\ \mu$ than for $2.098\ \mu$, which is quite an unexpected result. This cannot be explained by absorption effects, since they would influence the carbon radiation equally; neither does it seem to be a mere observational error since there is a definite and smooth progression. Possibly the explanation is to be found in a peculiarity of the energy curve such as an emission band in this neighborhood, but further investigation will be necessary before definite conclusions can be reached.

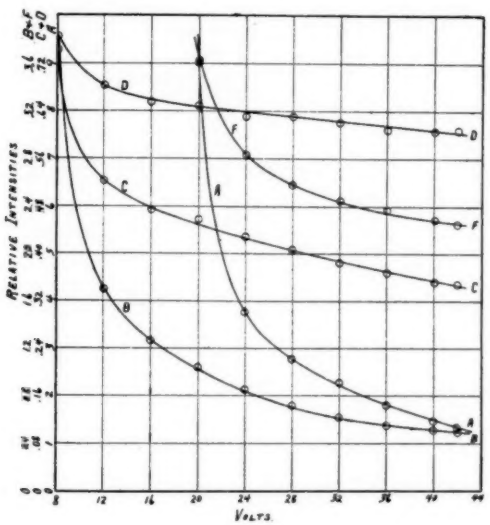


Fig. 5.

Energy Distribution, Osmium No. 1. Intensities relative to $I_{\lambda=2.098\mu}$. Curve *A*, .608 μ; Curve *B*, .726 μ; Curve *C*, 1.068 μ; Curve *D*, 1.750 μ; Curve *F*, 2.400 μ.

Application of Hyde's Criterion.—From Fig. 5 showing the variations of intensity ratios for the osmium lamp it is at once apparent that no voltage can be found at which the energy curve from this lamp will be of the same shape as that from the carbon lamp at any of the measured voltages. Hence criterion I. cannot be applied to this spectral region as a whole, but only at particular pairs of wave-lengths and temperatures.

Choosing $\lambda = 2.098\ \mu$ for comparison with each of the other wave-lengths, and, as before, temperatures corresponding to voltages for

TABLE VIII.

Isochromatic Intensity Ratios for Wave-Lengths and for Pairs of Voltages at which the Ratios ($I_{\lambda=2.098\mu} \div I_{\lambda'}$) are the Same for Both Lamps.

Wave-length.	Intensity Ratios ($I_{\lambda=2.098\mu} \div I_{\lambda'}$)		Carbon Lamp Voltages.		Osmium Lamp Voltages.		$I_{\lambda'}$ for Carbon No. 1.			$I_{\lambda'}$ for Osmium No. 1.		
	At Lower Voltage.	At Higher Voltage.	Lower.	Higher.	Lower.	Higher.	Lower.	Higher.	Ratio.	Lower.	Higher.	Ratio.
.608	6.25	3.68	180	220	21.20	24.30	12.2	29.7	.410	1.55	4.60	.337
	5.96	3.68	190	220	21.35	24.30	14.2	29.7	.478	1.60	4.60	.348
	6.25	4.39	180	210	21.20	22.90	12.2	23.1	.528	1.55	3.50	.443
.726	1.50	.935	180	220	13.60	22.20	51.0	117.0	.436	4.7	15.7	.299
	1.3	.935	190	220	15.45	22.20	63.6	117.0	.544	6.5	15.7	.414
	1.50	1.05	180	210	13.60	19.90	51.0	96.2	.531	4.7	12.0	.392
1.068	.525	.456	180	220	11.90	19.20	145.5	240.0	.606	10.4	26.0	.400
	.503	.456	190	220	13.50	19.20	168.5	240.0	.702	13.7	26.0	.527
	.525	.473	180	210	11.90	16.80	145.5	214.4	.678	10.4	20.7	.502
1.750	.700	.660	180	220	10.85	15.40	109.0	166.0	.657	6.6	13.0	.508
	.690	.660	190	220	11.55	15.40	122.8	166.0	739	7.5	13.0	.577
	.700	.674	180	210	10.85	13.12	109.0	150.5	.725	6.6	9.8	.674
2.400	2.43	2.58	180	220	33.30	28.25	31.3	42.2	.740	10.6	8.4	1.26
	2.48	2.58	190	220	31.25	28.25	34.1	42.4	.805	10.	8.4	1.21
	2.43	2.56	180	210	33.30	28.80	31.3	39.6	.790	10.6	8.7	1.22

The fulfillment of Criterion I would be indicated by the agreement of the ratios in columns 10 and 13.

carbon no. 1 of 180 and 220, 180 and 210, and 190 and 220, the intensity ratios which form the right hand members of equations (2) and (3) respectively may be found in Table VII. These are rearranged for convenience in Table VIII., columns 2 and 3. From Fig. 5 the voltages of the osmium lamp for which the same ratios hold may be determined, so that equations (2) and (3) are satisfied at these voltages (Table VIII., columns 6 and 7). Fig. 4 and similar curves give the intensities for the two lamps for these voltages at the chosen wave-lengths, and the isochromatic ratios of these intensities for any two temperatures form the two members of equation (4), which constitutes criterion I. These ratios appear in columns 10 and 13 of Table VIII., which should agree, according to equation (4). The wide discrepancy shows marked changes of emissivity with temperature, the greatest relative differences occurring in the neighborhood of the maximum of the energy curve, which is about 1.0 μ.

The peculiarity of osmium radiation at 2.400 μ already noted is here again evident, for at this wave-length when the carbon voltage is increased, that of osmium must be decreased in order to maintain the same relative intensities for wave-lengths 2.098 μ and 2.400 μ.

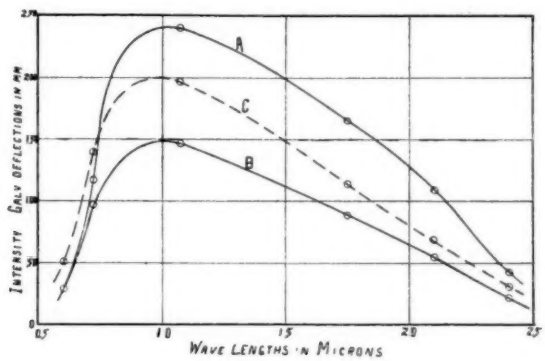


Fig. 6.

Approximate Spectral Energy Curves for Osmium and Carbon. Curve *A*, Carbon No. 1 at 220.0 volts; Curve *B*, Osmium No. 1 at 35.97 volts; Curve *C*, Osmium No. 1 at 42.00 volts; Curves *A* and *B* at color match temperatures.

Relative Selectivity of Osmium and Carbon.—The isochromatic curves of Fig. 4 supply the data necessary for a comparison of the energy curves for osmium and carbon when the two are at a color match in the visible region. Table IX. shows the deflections at various wave-lengths for both lamps corresponding to a color match with the carbon at 220 volts. All the deflections for the observations on osmium were reduced to the

TABLE IX.

Comparison of the Spectral Energy Distribution in the Infra-red for Carbon No. 1 and Osmium No. 1.

Lamp.	Volts.		Deflections at Wave-lengths.					
			.608μ	.726μ	1.068μ	1.750μ	2.098μ	2.400μ
C no. 1	220		29.7	117.0	240.0	166.0	109.6	42.4
O no. 1	35.97	Observed:	17.25	56.4	85.3	51.7	31.6	13.3
		Reduced:	29.7	97.0	147.0	89.0	54.4	22.9
O no. 1	42.00	Observed:	29.5	81.5	114.5	66.0	40.2	17.8
		Reduced:	50.8	140.5	197.2	113.8	69.3	30.6

same scale as the carbon deflections by a constant factor, viz., the ratio of the deflections at $\lambda = .608\ \mu$, since, the visible spectra matching, these ordinates should be equal. The deflections for carbon and the reduced

deflections for osmium are plotted in Fig. 7. The curve for osmium at 42 volts is also plotted to the same scale. No attempt has been made to locate exactly the maxima of these curves, nor have corrections been made for absorption, but the very large effect of selectivity is at once apparent in the depression of the osmium curves relative to those of carbon throughout the infra-red region. Even at 42 volts the osmium radiates less than the carbon for wave-lengths greater than 0.8 μ, although the former is far above the temperature for color match in the visible spectrum.

IV. SUMMARY.

Three incandescent lamps with osmium filaments have been studied. Data are presented and equations derived for the variations with voltage of the power consumed and the candle power radiated, and the functional dependence of current and watts per candle power upon voltage is indicated.

The luminous efficiencies of osmium and carbon lamps at color match voltages are compared, showing that osmium as a radiator is highly selective. Hyde's criterion for the detection of variations of emissivity with temperature has been applied both photometrically and spectrophotometrically, carbon lamps being used as comparison sources. Without exception all the results show that the emissivity is a function of both wave-length and temperature. A method is described for determining the relative shapes of the energy curves for two filaments when the best possible color match has been obtained, and the color ratios computed under various conditions indicate that, when the extremes are matched, the curve for osmium is somewhat depressed relative to that for carbon in the middle portion of the visible spectrum.

Energy curves for both radiators have been obtained in the infra-red region out to wave-lengths of 2.4 μ, and the observations show that the two cannot be brought into coincidence at any voltage. An application of criterion I. to these data again shows marked changes of emissivity with temperature. The relations of the energy curves in the infra-red at voltages corresponding to a color match in the visible spectrum are shown, the osmium radiation being very noticeably deficient in energy of the longer wave-lengths.

It has been shown that, within the range of observations presented, the rate of increase of intensity with temperature increases from the longer toward the shorter wave-lengths for the carbon filament, but that for the osmium in the neighborhood of 2.4 μ the rate of increase is greater than for wave-lengths 2.098 μ or 1.750 μ. An explanation of

this effect as indicating an emission band is suggested, though this has not been verified.

In conclusion the writer wishes to express his indebtedness to Dr. K. E. Guthe for his continual interest and helpful suggestions; also to Dr. E. P. Hyde for loaning the osmium lamps used and the standard sectored discs for calibration purposes.

PHYSICAL LABORATORY,
UNIVERSITY OF MICHIGAN,
May 1, 1915.

THE OPTICAL ACTIVITY OF LIQUIDS AND GASES.

BY FRANK GRAY.

THE natural activity of isotropic substances has been an interesting subject both to the chemist and to the physicist. Each has attacked the problem according to his own particular method; but unfortunately, the two lines of attack have not met. On the chemical side Pasteur, Le Bel and van't Hoff developed the present conception of molecular structure and proposed the theory connecting optical activity with an asymmetric structure of the molecule, a theory confirmed by the enormous amount of experimental work carried out in recent years. In the domain of physics the subject has been treated more from the optical view point and Drude and Voigt have shown just what form of electro-magnetic equations must hold in an active medium in order to produce rotation. However, the two theories have not been tied together; it has not been shown why the asymmetric molecule should give rise to these particular equations.

It was for this reason that the present study of optical activity was taken up. Part I. of the present paper is a brief report of a theoretical study of a few types of molecules, a study which has led to a very natural and satisfactory explanation of both the chemical and the physical facts of optical activity. Part II is a report of an experimental search for phenomena predicted from the theory.

PART I. THEORETICAL.

In the three-dimensional formulæ of chemistry, a symmetrical molecule is one that can be divided into two similar halves by a single plane, an asymmetrical molecule cannot so be divided. An enormous amount of work has been done on molecular structure by other methods than those of optical activity and the results have supported the theory that only an asymmetrical molecule can cause rotation.

If we accept, in general, the three-dimensional formulæ as representing molecular structure, then the experimental facts of optical activity may be stated as follows:

1. Any substance whose molecules are asymmetrical causes rotation. This is true for all carbon compounds, internal compensation and indirect asymmetry giving rise to only apparent exceptions.[1] Rotation has also

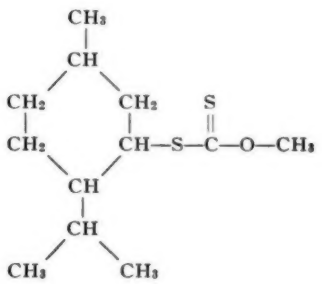
[1] "Stereo Chemistry," A. W. Stewart, 44, 83, 105.

been observed in compounds of nitrogen, sulphur, selenium, tin, and silicon.

2. Antipodes, a molecule and its mirror image, rotate in opposite directions.

3. Symmetrical molecules are not active,[1] pseudo-asymmetry and a few other cases are only apparent exceptions.

4. Absorption systems in an active substance cause anomalies in the rotary dispersion, although the origin of the band may lie in a part of the molecule distant from the central carbon atom.[2] Thus for example, in the menthyl ester of methyl dithio carbonic acid the asymmetric atom is in the ring group, while the absorption center is in the group $S = C$.



5. The magnitude of the activity is profoundly influenced by the molecular structure and is roughly dependent on the magnitude of the asymmetry of the molecule.

6. Activity varies with temperature[3] and pressure, and with the concentration of active molecules.

In attempting to account for the general facts of optical activity, new terms have been added to the field equations.[4] Thus Dude, Voigt, and Lorentz write the first equation for an active medium

$$\text{(1)} \qquad \text{curl } H = \frac{\mathrm{I}}{C}(\epsilon \dot{E} - f \,\text{curl}\, \dot{E}),$$

according to Lorentz the second field equation remains unchanged,[5]

$$\text{(2)} \qquad \text{curl } E = -\frac{\mathrm{I}}{C}\dot{H}.$$

[1] "Stereo Chemistry," A. W. Stewart, 21.

[2] Cotton, Ann. Chim. et d. Phys., 8, 374, 1896. Tuchugaff and Ogordnikoff, Zeit. für Phys. Chem., 74, 503, 1910, and 85, 481, 1913.

[3] Landolt, "Optical Rotation of Organic Substances," 206.

[4] Landolt, "Optical Rotation of Organic Substances," 169.

[5] Lorentz, Versuch einer Theor. der elekt. und optik. Erscheinungen.

Drude and Voigt have decided from energy considerations that the second equation should be

$$\text{curl } E = -\frac{1}{C}\left(\dot{H} + \frac{f}{C}\ddot{E}\right). \tag{3}$$

The solution of 1 with either 2 or 3 for a plane polarized wave shows that the electric vector E is rotated as the wave passes through the medium, the amount of the rotation being half as great when the Lorentz equations are used.

For the case of a plane polarized light wave these equations may be interpreted as stating that a space rate of change of E in the direction of propagation produces a component of electric polarization normal to both E and the direction of propagation, a component that does not exist in a non-active medium. In the following work we shall denote this component by P_n.

Drude has shown that the modified field equations would result if the paths of some of the electrons in an active medium were short helices all twisted in the same direction and with axes oriented at random in space, but he made no attempt to show how the asymmetrical structure of the molecule causes these spiral tracks, and thus his theory does not tie up with molecular structure, nor does it account for the anomalous rotary dispersion of the metallic tartrates and such cases as the one mentioned above. It was for this reason that the following study of the interaction between atoms was made in the hope that such interactions might afford a more satisfactory explanation of optical activity.

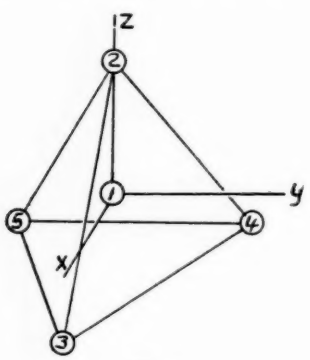


Fig. 1.

A Molecule of Five Atoms.

Consider a molecule consisting of a central atom with four other atoms grouped about it. The origin of a coördinate system (Fig. 1) will be taken at the central atom, and the axes so oriented that atom 2 will lie on the z axis and atom 3 in the xz-plane. The position of the nth atom is determined by x_n, y_n, z_n, and its distance from the origin by r_n. The distance from the nth to the mth atom is d_{nm}.

It is assumed that the atoms may be electrically polarized in any direction by an electric force and that

$$p_{xn} = K_n E_x, \text{ etc.}, \tag{4}$$

where p_{xn} is the x component of polarization of the nth atom and K_n is a quantity depending on the atom, the molecule in which the atom occurs, and on the frequency of the wave. K_n is to be thought of as the restoring coefficient that would exist if the nth atom could be made to oscillate electrically while all the other atoms remained unpolarized. It, therefore, does not contain any terms depending on the interactions of the electrical oscillations of the atoms, but it might contain terms depending on the static forces that hold the atoms together. For mathematical simplicity it is also assumed that the atoms are small compared to the distances between them; the atoms may thus be treated as electric doublets.

When a train of light waves passes over such a molecule it will tend to polarize the atoms in the E direction. The polarized atoms will then interact in a complicated manner, and as a result the molecule as a whole will not be polarized directly in the direction of the original E of the wave and the plane of vibration of the wave will be twisted a little out of its original direction. A molecule with some other orientation may twist the plane of vibration in the opposite direction. The problem is to determine if there will be any resultant rotation when plane polarized light passes through an aggregate of such molecules oriented at random in space.

The method of attacking the problem will be to find the component of polarization of a single molecule in the N direction, *i. e.*, normal to E and the direction of propagation, and then find the average of this component for all orientations of the molecule. The polarization P_n of the medium will be found by multiplying this average value by the number of active molecules per unit volume. The polarization of the medium in the E direction will be found in the usual manner. Thus the polarization of the medium will be completely known and it should be possible to write out the field equations which will hold in the medium for a plane polarized light wave. It is evident that if P_n is different from zero the medium will be active.

The vector expressions[3] for the forces at a distance r from an oscillating doublet are

$$E = \frac{1}{r^3}\{3p_r r_1 - p\} + \frac{1}{r^2}\{3\dot{p}_r - \dot{p}\} - \{\ddot{p}r_1 - p\} \tag{5}$$

$$H = -\frac{1}{r^2}[r_1\dot{p}] - \frac{1}{r}[r_1\ddot{p}],$$

where p_r is the polarization in the r direction and r_1 is a unit vector in the

[1] Drude, Gött. Nachr., 1904, I., 1.
[2] Drude, "Lehrbuch der Optik," 338.
[3] Abraham, "Theorie der Elektrizatät," II., 63.

r direction. Since r is small compared to the wave-length of light, all terms but the $1/r^3$ terms will be neglected. This term is only the ordinary electro-static force of a doublet. Let p_{xm}, p_{ym}, p_{zm} be the components of polarization of the mth atom whose coördinates are x_m, y_m, z_m, and let d_{nm} be the distance to the nth atom whose coördinates are x_n, y_n, z_n. Then, the components of force at atom n due to the polarization of atom m are

$$E_x = \frac{1}{{d_{nm}}^3}\left\{\frac{3}{{d_{nm}}^2}(x_n - x_m)[p_{xm}(x_n - x_m) + p_{ym}(y_n - y_m) + p_{zm}(z_m - z_n)] - p_{xm}\right\},$$

$$E_y = \frac{1}{{d_{nm}}^3}\left\{\frac{3}{{d_{nm}}^2}(y_n - y_m)[\cdots] - p_{ym}\right\}, \tag{6}$$

$$E_z = \frac{1}{{d_{nm}}^3}\left\{\frac{3}{{d_{nm}}^2}(z_n - z_m)[\cdots] - p_{zm}\right\}.$$

Let x', y', z' be a fixed coördinate system to which the plane polarized light wave is referred. The z' axis will be taken in the direction of propagation, the x' axis in the E direction, and the y' axis in the N direction. The x, y, z system in which the molecule is fixed, will be referred to the x', y', z' system by the angles ϕ, β, θ of Fig. 2.

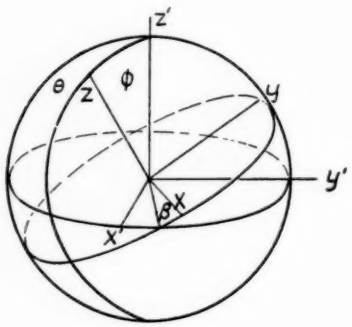


Fig. 2.

Let the electric force of the wave be given at the origin by

$$E_{x'} = E_{x'} \cos \nu t, \text{ etc.}$$

Then the external force on the nth atom is

$$E_{x'} = E_{x'} \cos\left(\nu t - \frac{\nu}{c} z_n'\right), \text{ etc.} \tag{7}$$

The total force acting on an atom has the same period as the wave; so the polarization of the mth atom may be written

$$\begin{aligned} p_{xm} &= P_{xm} \cos(\nu t - \delta_{xm}), \\ p_{ym} &= P_{ym} \cos(\nu t - \delta_{ym}), \\ p_{zm} &= P_{zm} \cos(\nu t - \delta_{zm}). \end{aligned} \tag{8}$$

The electro-static action of one atom upon another will be retarded, thus the force exerted upon atom n by atom m at the time t will be due to the retarded state

$$p_{xm} = P_{xm} \cos\left(\nu t - \delta_{xm} - \frac{\nu}{c} d_{nm}\right), \text{ etc.} \tag{9}$$

In the equation for the polarization of an atom,

$$\frac{1}{K_n} p_{xn} = E_x, \text{ etc.,} \tag{4}$$

the electric force includes that of the wave and also the forces arising from each component of polarization of the other four atoms. Using equations 6, 7 and 9 to determine the total force acting on an atom n, equation 4 becomes

$$\begin{aligned}\frac{1}{K_n}\cos(\nu t - \delta_{xn}) &= E_x \cos\left(\nu t - \frac{\nu}{c} z_n'\right) \\ &+ \sum_{m=1}^{5} \frac{1}{d_{nm}^3}\left[\frac{3(x_n - x_m)^2}{d_{nm}^2} - 1\right]\cos\left(\nu t - \delta_{zm} - \frac{\nu}{c} d_{nm}\right) P_{zm} \\ &+ \frac{3}{d_{nm}^2}(x_n - x_m)(y_n - y_m)\cos\left(\nu t - \delta_{ym} - \frac{\nu}{c} d_{nm}\right) P_{ym} \\ &+ \frac{3}{d_{nm}^2}(x_n - x_m)(z_n - z_m)\cos\left(\nu t - \delta_{zm} - \frac{\nu}{c} d_{nm}\right) P_{zm},\end{aligned} \tag{10}$$

where the summation excludes the nth atom. After expanding the cosine terms, the equation reduces to

$$(\cdots)\cos \nu t + (\cdots)\sin \nu t = 0.$$

The quantities inside the bracket are independent of t; therefore each must be equal to zero. If we let

$$P_{zm}\cos\delta_{zm} = A_{zm},$$
$$P_{zm}\sin\delta_{zm} = B_{zm},$$

these conditions are expressed by the equation

$$\begin{aligned}\frac{1}{K_n} A_{zn} &= E_x \cos\frac{\nu}{c} z'_n + \sum_{m=1}^{5} \frac{1}{d_{nm}^3}\cos\frac{\nu}{c} d_{nm}\left\{\left[\frac{3(x_n - x_m)^2}{d_{nm}^2} - 1\right] A_{zm}\right. \\ &\left. + \frac{3}{d_{nm}^2}(x_n - x_m)(z_n - z_m) A_{ym} + \frac{3}{d_{nm}^2}(x_n - x_m)(z_n - z_m) A_{zm}\right\} \\ &- \frac{1}{d_{nm}^3}\sin\frac{\nu}{c} d_{nm}\left\{\left[\frac{(3x_n - x_m)^2}{d_{nm}^2} - 1\right] B_{zm} + \frac{3}{d_{nm}^2}(x_n - x_m)(y_n - y_m) B_{ym}\right. \\ &\left. + \frac{3}{d_{nm}^2}(x_n - x_m)(z_n - z_m) B_{zm}\right\},\end{aligned}$$

and a similar one for $1/K_n(B_{zn})$ in sine terms but with the A's and B's interchanged. There are thus thirty linear equations to solve for the thirty A's and B's.

In forming the determinant the unknowns may be numbered as follows:

$$\begin{array}{cccccc} 1 & 2 & 3 & 4 & \cdots & 15 \\ A_{x1} & A_{y1} & A_{z1} & A_{x2} & & A_{z5}, \\ 16 & 17 & 18 & 19 & \cdots & 30 \\ B_{x1} & B_{y1} & B_{z1} & B_{x2} & & B_{z5}, \end{array}$$

and the equations may be numbered

$$(1) \qquad \frac{1}{K_1} A_{x1} = E_x \cos \frac{\nu}{c} z_1' + \Sigma$$

$$(2) \qquad \frac{1}{K_1} A_{y1} = \text{————————}$$

. . . . . .

$$(15) \qquad \frac{1}{K_5} A_{z5} = \text{————————}$$

$$(16) \qquad \frac{1}{K_1} B_{x1} = \text{————————}$$

. . . . . .

$$(30) \qquad \frac{1}{K_5} B_{z5} = \text{————————}.$$

The following relations hold among the minors of the general determinant. If D_r^h is the minor formed by suppressing the rth row and the nth column, then

$$\begin{aligned} D_r^h &= D_h^r, \\ D_r^h &= D_{h+15}^{r+15}, \\ D_r^h &= -D_{r+15}^{h-15}, \\ D_{r+15}^h &= -D_{r+5}^h, \\ D_{r-15}^{h+15} &= D_r^h. \end{aligned}$$

The value of any unknown, number m, may be found by substituting the constants for the mth column and dividing by D. The following is the solution for A_{x1} after expanding the numerator by minors with respect to the column of constants.

$$\begin{aligned} A_{x1} = \frac{1}{D} \Big\{ & E_x D_1^1 - E_y D_1^2 + E_z D_1^3 - E_x D_1^4 \cos \frac{\nu}{c} z_2' \\ & + E_y D_1^5 \cos \frac{\nu}{c} z_2' + \cdots E_x D_1^{16} + E_y D_1^{17} - E_z D_1^{18} \\ & + E_x D_1^{19} \sin \frac{\nu}{c} z_2' - E_y D_1^{20} \sin \frac{\nu}{c} z_2' + \cdots \Big\}. \end{aligned}$$

There will be similar solutions for all the other A's and B's.

If the solution A_{xm} be multiplied by cos νt and that of B_{xm} by sin νt and combined using the relation between minors given above and also letting

$$R_r^h = \sqrt{(D_r^h)^2 + (D_r^{h+15})^2},$$

then

$$P_{xm} = \frac{1}{D}\left\{ \sqrt{2}[\pm E_x R_m' \cos(\nu t - \epsilon) \pm E_y R_m^2 \cos(\nu t - \epsilon) \pm E_z R_m^2 \cos(\nu t - \epsilon)] \pm E_x R_m^4 \cos\left(\nu t - \frac{\nu}{c} z_2' - \epsilon\right) \pm \cdots \right\}, \tag{11}$$

where all the ϵs are different. An example of one ϵ is

$$\epsilon = \tan^{-1} \frac{D_1^5}{D_1^{20}}.$$

It is found that the ϵs do not occur in the final result, and they are thus of little interest.

The undetermined signs of equation 11 could be determined in an actual case by going back to the physical meaning of equation 3. Even in the present general case the sign of a great many of the terms may be found. There are fifteen such equations, one for each component of polarization of the five atoms.

The total polarization of the molecule in the N direction, *i. e.*, $P_{y'}$ may be found by projecting the components of polarization of each atom on the y' axis and taking the sum for all atoms in the molecule. The average of this polarization $\overline{P_{y'}}$ for molecules oriented at random, may be shown to be

$$\overline{P_{y'}} = \frac{1}{8\pi^2} \int_0^{2\pi} d\phi \int_0^{2\pi} d\beta \int_0^{\pi} P_{y'} \sin\theta d\theta,$$

where, of course, $P_{y'}$ will be a function of ϕ, β, θ. Before integrating it is necessary to express E_x, E_y, E_z occurring in $P_{y'}$ in terms of $E_{y'}$ and also to express z_n' in terms of x_n, y_n, z_n.

In order to carry out the integration the following approximation is made

$$E_{x'} \cos\left(\nu t - \frac{\nu}{c} z_m' - \epsilon\right) = E_{x'} \cos(\nu t - \epsilon) - \frac{\partial E_{x'}}{\partial z'} z_n', \text{ etc.}$$

It may be shown that ϵ expresses the lag of the retarded interaction behind the E of the wave and that it is very small compared to 2π. So $\partial E_{x1}/\partial z'$ will be practically constant for such a short time and the approximation is justified.

There will be 225 terms in $\overline{P_{y1}}$ similar to

$$\frac{1}{8\pi^2}\int_0^{\pi} d\varphi \int_0^{\pi} d\theta \int_0^{2\pi} \frac{R_m{}^4}{D}(\cos\phi\cos\theta\cos\beta - \sin\beta\sin\theta)(\cos\beta\cos\phi\sin\theta + \sin\phi\cos\theta)\left\{E_{x'}\cos(\nu t - \epsilon) - \frac{\delta E_{x'}}{\partial z'}(-x_2\cos\beta\sin\varphi + y_2\sin\beta\sin\varphi + z_2\cos\varphi\right\}\sin\varphi\, d\beta.$$

In the integration all terms will vanish except certain ones containing $\partial E_{x1}/\partial z'$. The final result is

$$\overline{P_y'} = \frac{1}{12D}\frac{\partial E_{x'}}{\partial z'}[z_2\{(\pm R_1{}^5 \pm R_2{}^4) \pm (R_7{}^5 \pm R_8{}^4) \pm (R_{10}{}^5 + R_{11}{}^4) \pm (R_{13}{}^5 + R_{14}{}^4) + x_3\{\cdots\} + z_3\{\cdots\} + \cdots + z_5\{\pm (R_1{}^{14} + R_2{}^{13}) \pm (R_4{}^{14} + R_5{}^{13}) \pm (R_7{}^{14} + R_8{}^{13}) \pm (R_{10}{}^{14} + R_{11}{}^{13})\}]. \tag{12}$$

It may be shown that this expression is not identically equal to zero. Thus $\overline{p_{y'}}$ will, in general, be different from zero and the medium will have a component of polarization in the N direction. As stated previously, this means that the medium will be active.

In equation 12 let

$$b = \frac{1}{12D}[\cdots],$$

then

$$\overline{P_{y'}} = b\frac{\partial E_{x'}}{\partial z'}.$$

If n is the number of active molecules per unit volume, then the polarization in the N direction will be

$$P_H = nb\frac{\partial E_{x'}}{\partial z'}.$$

This is for the special case of axes x', y', z' taken in the direction of propagation of the wave and in the H and E directions respectively. For any set of axes this equation may be shown to be

$$P_H = nb\ \text{curl}\ E.$$

The polarization in the E direction is

$$P_E = E\Sigma\frac{e^2/m}{\nu_0{}^2 - \nu^2} = E\Sigma,$$

Where ν_0 is the natural frequency of an electron in the medium, e is the electronic charge, and m is the electronic mass. The summation is taken over all electrons in unit volume. It is to be noted that this summation is the same one that occurs in the theory of refractive indices and that it is taken over both active and non-active molecules in the

medium. The interaction between atoms in the same molecules has been taken care of in ν_0, for ν_0 means the frequency of an electron as it occurs in the molecule and not the frequency it would have in the isolated atom.

The total polarization is

$$P = P_N + P_E = E\Sigma + nb \operatorname{curl} E.$$

In this equation we have neglected the fact that the force acting on an electron in a material medium is really not E but $E + aP$, where a is usually considered to be about $4\pi/3$. Putting in this additional term

$$P = (E + aP) + nb \operatorname{curl} (E + aP).$$

Then,

$$P = E\frac{\Sigma}{1 - a\Sigma} + \frac{nb}{1 - a\Sigma}\operatorname{curl} (E + aP).$$

Put

$$P = E\frac{\Sigma}{1 - a\Sigma}$$

in the curl term; then

$$P = E\frac{\Sigma}{1 - a\Sigma} + \frac{nb}{(1 - a\Sigma)^2}\operatorname{curl} E.$$

The first field equation then becomes

$$\operatorname{curl} H = \frac{1}{c}\left(1 + 4\pi\frac{\Sigma}{1 - a\Sigma}\right)\dot{E} + \frac{4\pi}{c}\frac{nb}{(1 - a\Sigma)^2}\operatorname{curl} \dot{E},$$

and according to equation 3, the second equation should be

$$\operatorname{curl} = -\frac{1}{c}\dot{H} - \frac{8\pi}{c^2}\frac{nb}{(1 - a\Sigma)^2}\ddot{E}.$$

The solution of the two equations gives for the rotation per unit length

$$\delta = -\frac{4\pi nb}{(1 - a\Sigma)^2}\frac{\nu^2}{c^2}. \tag{13}$$

According to Lorentz, equation 2, the second field equation remains unchanged and the rotation should be half as great.

Antipodes.

It may be shown that antipodes rotate in opposite directions. The antipode of the present general molecule of five atoms may be easily treated by interchanging the positions of atoms 4 and 5 with respect to the xz-plane but letting each atom keep the same absolute valueof coördinates. If the present system of coördinates is changed into a

left-handed system by reversing the y and y' axes and measuring θ and β in a left-handed sense, then all equations will hold identically in the left-handed system; so $\overline{p_y'}$ will be given by equation 12. But, with respect to the light wave, y' is now in the opposite direction to what it was for the first molecule, and the rotation will be opposite in sign but of the same magnitude as before.

The Symmetrical Molecule.

The symmetrical molecule may be most easily considered by letting atoms 4 and 5 be identical; then

$$x_4 = x_5$$
$$|y_4| = |y_5|$$
$$z_4 = z_5$$
$$K_4 = K_5.$$

From a consideration of the general determinant it may be shown that a great many of the Rs in Eq. 12 vanish and the remainder cancel out leaving $\overline{p_y'} = 0$. So a symmetrical molecule cannot cause rotation.

Other Molecules.

The case of a molecule containing less than five atoms is obtained by setting $K = 0$ for one or more atoms. It is found that:

A molecule of only two atoms cannot be active.

A molecule of three atoms cannot be active.

An asymmetrical molecule of four atoms would be active.

However, a molecule of this type is not known. Every known molecule of four atoms consists of a central trivalent atom with three other atoms attached to it; thus all four atoms probably lie in the same plane or at least oscillate back and forth through the same plane. In either case the molecule would be inactive. This is supported by the failure to resolve such compounds into isomeric forms.

A treatment similar to the present could be extended to molecules of more than five atoms; and from analogy with the present case it seems probable that an asymmetric molecule will be active and a symmetrical molecule inactive.

Rotatory Dispersion.

The K for an atom is the polarization of the atom by unit electric field and it may be shown that

$$K_n = \Sigma \frac{e^2/m}{\nu_0^2 - \nu^2},$$

where the summation is taken over all electrons in the nth atom. Thus K will vary with the frequency of the wave and cause rotatory dispersion. At an absorption band whose origin is in an active molecule, one of the Ks will pass through anomalous values and change sign. The factor b in equation 13 is an algebraic function of the Ks; thus we might, in general, expect the rotation to be anomalous at a band, but not necessarily in the simple manner demanded by the Drude theory. This is in agreement with the rotatory dispersion of the metallic tartrates and malates. It is conceivable that the general rotatory dispersion of a substance might prevent an absorption band from producing an anomaly just as in the case of ordinary dispersion a band does not always produce anomalous dispersion.

Bruhat[1] has shown that the term $(1 - \Sigma)^2$ in Eq. 13 cannot cause an appreciable anomaly in ordinary cases. The absorption coefficient must be of the order of that for metallic absorption before this term becomes important.

Rotation and Atomic Refractivity.

The Ks are closely connected with atomic refractivities. The molecular refractivity of a substance is defined as

$$M = \frac{m}{d}\frac{n^2 - 1}{n^2 + 1} = \text{constant.} \quad \Sigma \frac{e^2/m}{\nu_0^2 - \nu^2},$$

where m is the molecular weight; d, the density; and n is the refractive index. The atomic refractivity is the contribution of each atom to this sum. In many organic compounds the atomic refractivities are approximately additive and, in such cases, the Ks are proportional to the atomic refractivities. In complex molecules it often happens that the atomic refractivities are not additive, but the summations over closely built groups are additive, and in such cases we may think of K for the whole group as being proportional to its group refractivity. There should thus be a close connection between atomic or group refractivity and optical activity; a radical with a large group refractivity should exert a greater influence upon the activity of a molecule than a radical with a smaller group refractivity.

This is well shown by the influence of the double ethylene bonding $C = C$ upon the activity of a molecule. It is well known that an ethylene group introduced into a molecule produces an abnormally high molecular refractivity, and Walder and Zilnsky[13] have shown that such a group also tends to increase the molecular activity when introduced into a molecule.

[1] "Stereo Chemistry," Stewart, 98.

[2] Bruhat, Phil. Mag., 28, 302, 1914.

These considerations bring out clearly the reason for the failure of the Guye hypothesis[1] in so many cases. Roughly, this hypothesis states that the optical activity of a molecule is measured by its mass asymmetry. From the present theory it is evident that it is not the mass asymmetry that is important but the asymmetry in terms of atomic or group refractions that is important.

Change of Rotation with Temperature.

The activity of most substances varies rapidly with the temperature;[4] for some substances it increases; for others, it decreases and may even change sign. No attempt has been made to explain these bewildering changes, because of the lack of any adequate theory of rotation itself. There can be little doubt that, on account of thermal agitations, the atoms are vibrating about points of equilibrium inside of the molecule. However, on the Guye hypothesis, it was difficult to see how such oscillations could affect the rotation, for on the average the atom would act as if it were fixed at the position of equilibrium.

This is not true from the present point of view. The electrostatic action of two atoms varies as $1/d^3$. For such a law of force the average interaction will change with the amplitude of the oscillations and thus cause the rotation to vary with the temperature.

Without doubt other factors such as loose chemical changes also enter into the temperature effect.

PART II. EXPERIMENTAL.

On the Drude theory, only those electrons which vibrate along spiral paths give rise to anomalous rotation; on the present theory, any absorption band belonging to an electron in an active molecule might be accompanied by an anomaly. The work of Tuchugoff and Ogordnikoff referred to in the first part of this paper may be looked upon as supporting this view. It is well known that certain atomic groups called chromophores act as absorbing centers and that a colored compound is produced when one is introduced into the molecule of an otherwise colorless substance. These two experimenters have united non active radicals containing the chromophore $C = S$ with complex active radicals, and they find that the absorption bands of the resulting compounds show anomalous rotation. Although the absorption in such cases is always connected with the chromophores, the appearance and position of the band is characteristic of the molecule. So it was decided that a more severe test of the theory was desirable, and this test was carried out in the following manner.

[1] Landolt, "Optical Rotation of Organic Substances," 299.

The group of neodymium absorption bands near 5,800 and 5,200 are characteristic of the neodymium atom and are not greatly influenced by the molecule in which the atom is present. The electrons causing these bands do not vibrate along spiral paths, for such compounds as neodymium nitrate are inactive. If this atom is united with an active acid radical, will these electrons cause anomalous rotation? According to the present theory they might; while, according to the Drude theory it is difficult to see how they could cause anomalies, because they are little influenced by molecular structure.

Most organic salts of the rare earths are insoluble, but a soluble active compound of neodymium was finally obtained in the following manner. Neodymium nitrate was dissolved in a neutral solution of sodium tartrate and a crystalline substance separated out slowly. At the end of a week this was filtered off and was found to be soluble in a basic solution. Using sodium hydride the solution was made just basic enough to dissolve all the crystals. The solution was very dilute. The compound is probably a double tartrate of neodymium and sodium. It may be mentioned that the original nitrate was not very pure as it contained some lanthanum; however its presence was not objectionable in the present work.

The solution is strongly absorbing and it was difficult to measure the rotation inside of the absorption bands. As the general rotation for 8 cm. of the solution was only one degree and the absorption bands are relatively broad compared to those of a gas, it was impossible to use the quartz wedge method. It was finally decided to use a monochromatic illuminator with a divided field.

The usual form of monochromatic illuminator is not suitable for the purpose, because the maximum brightness that can be obtained for the divided field does not depend on the ratio of focal length to aperture of the collimating lens but only upon the dispersion and aperture of the prisms.[1] After several failures with different forms of apparatus, a powerful and rather simple instrument was constructed. The optical system is shown in Fig. 3. Two high dispersion prisms were used with auto-collimation to double the dispersion. The visible spectrum was spread out over almost thirty degrees of arc. The prisms were set at minimum deviation for the band to be examined and the spectrum was moved across the slit S_2 by rotating the mirror M. The collimating lens L_1 had a focal length of 52 cm. The lens L_2, of 28 cm. focal length, formed an image of a point behind the collimating lens on the divided field F and thus gave it uniform illumination. The image of the slit

[1]Elias, Zeit. fur Instrumentenkunde, 31, 137, May, 1911.

S_2 fell upon the pupil of the eye placed at the diaphragm D. The divided field was viewed directly without the aid of an eye piece, thus saving a loss of light by reflection. Maximum brightness was secured by making the apparent size of the illuminated area of F only just large enough for settings to be made and by always keeping the slits S_1 and S_2 of the same width. A cell 8 cm. long and containing the active solution was placed at C.

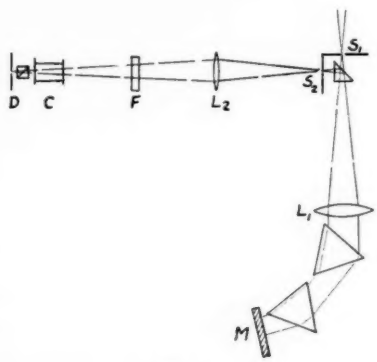


Fig. 3.

Scattered light was carefully screened out. It is impossible to get rid of all the light reflected from the collimating lens, but with the present arrangement all such light goes to form a small image of the slit, which appears as a speck in the divided field and thus causes no error.

An intensely bright field could be obtained, monochromatic to 2A°; but the absorption of the neodymium solution was so great that it was necessary to use 10 A° even with the brightest sun light. The 10 A° means the range of wave-lengths that could pass through the slit S_2 when the width of S_1 and S_2 were equal.

To prove that an apparent anomaly could not result from stray light or too great a slit width, the following test was made. A cell full of the neodymium solution was placed as an absorption cell just behind the slit of the monochromatic illuminator. An active sugar solution examined under these conditions showed no false anomaly, thus proving that there was no serious error from the two causes just named.

In the case of the original neodymium nitrate the absorption band in the yellow could be resolved into five lines: 5,716, a pair of strong lines 5,744 and 5,750, 5,784 and a weak line 5,807. There were two strong lines at 5,219 and 5,202. In the double tartrate the band in the yellow was shifted about 30 A° toward the red, and it could again be resolved into five lines: 5,733 weak, 5,770, 5,800 very strong, 5,819, 5,837. The band in the blue was shifted to 5,364 and could no longer be resolved into

two components. Such changes as these are to be expected for the same reason that a change of solvent will shift and change the character of the bands. However, the bands are so characteristic of the atom that it is to be supposed that no great change takes place in the mode of vibration of the electrons.

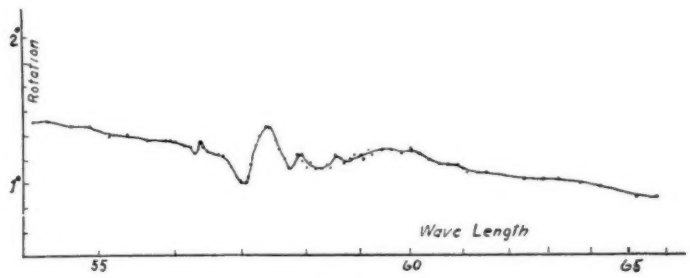


Fig. 4.

The curve shows the rotation of 8 cm. of the solution near the band 5,800.—With this depth of solution the five lines appear merged together. —The rotation is anomalous as predicted from the present theory. The large anomaly is apparently connected with the line 5,770 which is relatively weak. There are indications of anomalies in the strong absorption region covered by the three lines on the long wave-length side of the band. It is possible that larger anomalies really exist and that they have been smoothed over on account of the slit width of the illuminator. However, if all the lines tend to have anomalies of the same type, we should expect the effect to cancel out for such closely spaced lines. A small anomaly was found at 5,642, and subsequent examination showed a very faint absorption band at that wave-length. The strong band near 5,200 also showed an anomaly of the same type as the one at 5,800, but the absorption is too great for a satisfactory curve to be made.

As mentioned before, these results are in agreement with the present theory, but could hardly be explained on the Drude theory of spiral paths.

In conclusion the writer wishes to thank Professor Lehner, of the chemistry department, for his assistance in preparing an active compound of neodymium.

Summary.

Assuming that the atoms of a molecule may be electrically polarized by a light wave and that they then interact according to the ordinary laws for an electric doublet, it has been shown that the optical activity of isotropic substances may be explained as a result of such interactions.

From this view point, an asymmetric molecule will be active and a symmetrical molecule inactive. A molecule must have more than three atoms to be active.

A connection has been shown between molecular activity and atomic refractivity.

A possible explanation of the variation of rotation with temperature has been given.

According to the present view of activity any absorption band belonging to an active molecule might cause anomalous rotation.

This last statement has been tested experimentally in the most extreme case that could be obtained. A neodymium atom was introduced into an active molecule and the rotation was found to be anomalous at the bands characteristic of the atom, a result which supports the present theory.

Note.—After the theoretical part of the present paper had been completed and while the experimental work was being carried out, two excellent articles were published on the same subject by J. Stark and M. Born. Stark[1] suggested that natural activity might be explained as the result of the interaction of doublets; and later Born[1] published a mathematical treatment of the same subject. The present paper is simpler and therefore less rigorous. It may also, in a way, be looked upon as a special case of Born's more general theory; instead of an indefinite coupling the atoms have been coupled in a very definite manner. There are two important differences: (1) Born views a molecule as a system of coupled electrons, the coupling and the restoring forces being identical. In the present paper the atom is looked upon as a particle of dielectric. The atoms are coupled according to the ordinary laws for a doublet, and the restoring force on an electron is not identical with the coupling but may be influenced by it. This is supported by the fact that many absorption bands are roughly characteristic of the atom and that for many organic compounds the refractive index is an almost additive property. (2) Born neglected the retardation of the interaction between particles. This retardation might be important because the rotation depends only on a space derivative of E, *i. e.*, upon the variation of E from one side of a molecule to the other. However, the conclusions agree with those of Born, and the experimental result is a support to both theories.

In the Annalen der Physik, 48, 1, 1, September, 1915, C. W. Oseen has also presented a theoretical treatment of optical activity, very similar to that of Born.

PHYSICAL LABORATORY,
UNIVERSITY OF WISCONSIN.

[1] Stark, Jahrbuch der Rad. und Elektronik., 1914.

[2] M. Born, Phys. Zeit., 16, 251, July, 1915.

THE THEORY OF IONIZATION BY COLLISION.

I. THE DISTRIBUTION OF VELOCITIES OF THE ELECTRONS.

BY K. T. COMPTON.

Introduction.—The fundamental equation in any theory of ionization of gases by impact is

$$n = n_0 \frac{(\alpha - \beta)\epsilon^{(\alpha-\beta)d}}{\alpha - \beta\epsilon^{(\alpha-\beta)d}}, \qquad (1)$$

where n_0 is the number of negative ions which start per second from the negative electrode, n is the number per second which reach the positive electrode and α and β are the average numbers of new ions of either sign formed per centimeter path by each negative and positive ion respectively. In many cases the ionization is due almost entirely to the negative ions and equation (1) reduces to

$$n = n_0\epsilon^{\alpha d}. \qquad (2)$$

These equations were first proposed by Townsend[1] and are correct on any theory of ionization due exclusively to collisions. They afford no information concerning the mechanism by which impacts may result in the formation of new ions.

Attempts to derive, from assumptions regarding the nature of ionization, expressions for α and β in terms of properties of the colliding particles have not been very successful. Townsend[2] assumed that collisions of electrons with molecules are inelastic, that ionization occurs at an impact if the velocity of the electron exceeds a critical value characteristic of the gas and that no appreciable recombination or formation of "clusters" occurs within the range of electric fields and pressures used in the experimental tests. The resulting formula for α agreed so well with the facts then known that these assumptions have been rather generally accepted as at least approximately true. However we know now that the constants in Townsend's formula differ from the correct values in most cases by more than a hundred per cent., being in some cases too large and in others too small. Moreover the equation is not successful for small fields and in the case of helium (and probably the other inert gases) the plotted curves are not even of the right general shape.

[1] "Ionization of Gases by Collision," pp. 4, 41.

[2] Ibid., p. 23.

Campbell[1] recently pointed out an error in the derivation of Townsend's formula. The corrected equation conforms slightly better to the experimental results, but the difference is not great and the constants are still far from correct.

The most satisfactory equation for α which has been proposed was derived by Bergen Davis[1] on assumptions similar to Townsend's except that the necessary condition for ionization at an impact is that the colliding electron must possess a velocity whose component normal to the surface of the molecule (considered spherical) exceeds a critical velocity characteristic of the gas. For many gases this formula fits the facts acceptably over a wide range of pressures and gives much more accurate values of the constants than does Townsend's formula. But it also fails in the case of helium and the other inert gases. Moreover it will be shown that certain conditions exist in the ionized gas which necessitate a modification of Bergen Davis's formula.

It appeared to the writer that a study of the distribution of velocities of the ions in the gas under various conditions should be of value in forming a theory of ionization by collision. The present paper gives the more important results of a study of the velocity distribution. On this foundation expressions for α have been derived which conform more nearly to the facts than any formula yet suggested and which may be applied to the inert gases and to mixtures of gases. The derivation and discussion of these equations will be given in a later paper.

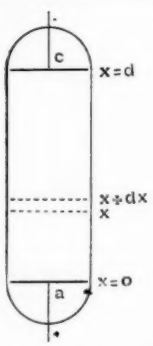


Fig. 1.

Notation.—For convenient reference the uniform notation employed is explained here. Let c be the cathode and a the anode in a discharge tube. By ultra-violet light, or otherwise, electrons are liberated from c and move toward a under the influence of the applied field. We shall let

x = distance from anode a measured in the direction of the potential drop;
d = distance between anode a and cathode c;
X = electric intensity (supposed uniform);
n_0 = number of electrons leaving c per second;
n = number of electrons passing plane x per second;
n_a = number of electrons reaching a per second;
ν = average number of collisions made by an electron in traveling one centimeter in the direction of the electric force;

[1] Phil. Mag., 23, p. 400 (1912).
[2] PHYS. REV., 24, p. 93 (1907).

P = probability that an electron ionizes when it collides;
P_x = probability that an electron goes a distance x without being stopped by a collision;
α = number of ionizing collisions by an electron per centimeter path;
β = number of ionizing collisions by a positive ion per centimeter path;
p = pressure of the gas;
e, m = charge and mass of an electron;
$F(v)dv$ = probability that an electron has a velocity between v and $v + dv$;
$F(x)dx$ = probability that it has moved freely a distance between x and $x + dx$;
$F(V)dV$ = probability that it has a velocity due to a potential drop between V and $V + dV$;
n', v', P', P_x' are the corresponding quantities which refer to the positive ions.

It has been recently shown,[1] as was previously suspected, that in some gases the electrons start approximately from rest after each collision while in others their kinetic energy is retained except at collisions which result in ionization. We shall call these cases of inelastic and elastic impact, respectively, and shall consider first the case of ionization by electrons only, which occurs when X/p and d are small. We shall be safe in assuming that no appreciable recombination or formation of "clusters" occurs within the range of pressures and electric fields employed in measurements of ionization by collision.[2]

A. Inelastic Impact.

(1) *Ionization Due Exclusively to Electrons.*

Consider the electrons colliding and originating in a layer dx distant x from the anode a (Fig. 1). The number of collisions per second in this layer is $nvdx$. Of these collisions, $Pnvdx$ result in the formation of new ions. Thus $(1 + P)nvdx$ ions start from rest in the layer dx each second. According to the kinetic theory of gases the probability that one of these will reach the anode a without further collisions is

$$P_x = \epsilon^{-\nu x}. \tag{3}$$

Thus

$$n_a F(x)dx = (1 + P)nv\epsilon^{-\nu x}dx$$

[1] Franck and Hertz, Verh. d. D. Phys. Ges., 15, p. 373 (1913); 16, p. 457 (1914).
[2] Townsend, Phil. Mag., 23, p. 856 (1912).

is the number of electrons reaching a per second after having traveled freely a distance between x and $x + dx$.

But in the layer dx the total number of electrons has been increased by the number $dn = -Pnvdx$, whence

$$n = n_a \epsilon^{-Pvx}. \tag{4}$$

Substituting this value of n we obtain

$$F(x)dx = (1 + P)v\epsilon^{-(1+P)vx}dx. \tag{5}$$

These reach a with a velocity determined by the relations

$$\tfrac{1}{2}mv^2 = eV = eXx; \tag{6}$$

whence

$$F(V)dV = (1 + P)\frac{v}{X}\epsilon^{-(1+P)\frac{vV}{X}}dV, \tag{7}$$

and

$$F(v)dv = (1 + P)\frac{vmv}{eX}\epsilon^{-(1+P)\frac{vmv^2}{2eX}}dv. \tag{8}$$

Now it is a well-known theorem in the kinetic theory of gases that the molecules which pass a plane in a gas have components of velocity normal to the plane whose distribution is given by an equation of the form

$$F(u)du = Au\epsilon^{-Bu^2}du.$$

By comparison with equation (8) it is seen that the electrons in the discharge tube reach the anode a with velocities distributed according to Maxwell's law. The average velocity with which they arrive is

$$v = \int_0^\infty vF(v)dv = \sqrt{\frac{\pi eX}{2(1 + P)vm}}$$

and the most probable velocity is

$$v = \sqrt{\frac{eX}{(1 + P)vm}}. \tag{9}$$

We have assumed here that the discharge tube is of infinite length. If it is of length d the initial velocity distribution $f(v)dv$ at c must be considered and the probability of ionization at a collision cannot be considered independent of x. Under these conditions an argument similar to that used to derive equation (8) leads to

$$F(v)dv = \left[\epsilon^{-v\left(d + \int_0^d Pdx\right)}f(v - v')\right]_{v=v'}^{v=\infty} + \left[(1 + P)\frac{vmv}{eX}\epsilon^{-\frac{vm}{eX}\left(\frac{v^2}{2} + \int_0^v Pvdv\right)}dv\right]_{v=0}^{v=v'}, \tag{10}$$

where v' is the velocity gained in a free passage from c to a. This expression reduces to equation (8) when d and v' are infinite and P is constant. The first term arises from those electrons which pass from c to a without suffering a collision and gives a velocity distribution identical with that of the emitted electrons increased by the amount v'. The second term gives the velocity distribution of those which have undergone collision or been produced in the gas and applies only to velocities less than v'. There is thus a discontinuity in the function $F(v)$ at $v = v'$.

Fortunately equation (10) becomes practically identical with (8) when d exceeds several mean free paths l. I have therefore used equation (8), or its equivalent (7), as the basis of part of the theory of ionization and in applying experimental results as a test I have rejected the few data taken under conditions in which equation (10) differs appreciably from (8). In the remainder of this paper we shall consider only cases in which d is at least several times greater than l.

(2) *Ionization Due Both to Electrons and to Positive Ions.*

In this case we have, as before, $(1 + P)n\nu dx$ electrons starting from rest in the layer dx every second as the result of collisions by electrons in this layer. In addition $P'n'\nu' dx$ electrons are formed per second by the impacts of positive ions. Thus $[(1 + P)n\nu + P'n'\nu']dx$ electrons start from rest in dx each second. Therefore

$$n_a F(x)dx = [(1 + P)n\nu + P'n'\nu']e^{-\nu x}dx \tag{11}$$

electrons arrive at a from dx each second.

But

$$dn = -[Pn\nu + P'n'\nu']dx = -[Pn\nu + P'(n_a - n)\nu']dx,$$

since of necessity $n_a = n + n'$ at any point in the gas. Integrating this equation we find

$$n = \frac{n_a}{(P\nu - P'\nu')}[P\nu\epsilon^{-(P\nu - P'\nu')x} - P'\nu'],$$

from which

$$n' = \frac{n_a}{(P\nu - P'\nu')}[P\nu - P\nu\epsilon^{-(P\nu - P'\nu')x}].$$

Substituting these values of n and n' in equation (11) and regrouping the terms we find that

$$F(x)dx = \frac{1}{(P\nu - P'\nu')}\{[(1 + P)P\nu^2 - P\nu P'\nu']\epsilon^{-[(1+P)\nu - P'\nu']x} - P'\nu'\nu\epsilon^{-\nu x}\}dx. \tag{12}$$

This equation of course reduces to (5) when $P' = O$ or $\nu' = O$.

By substituting for x from equation (6) we find that the distribution of velocities is given by

$$F(v)dv = \frac{(1+P)Pv^2 - PvP'v'}{Pv - P'v'} \frac{mv}{eX} \epsilon^{-[(1+P)v - P'v']\frac{mv^2}{2eX}} dv - \frac{P'v'v}{Pv - P'v'} \frac{mv}{eX} \epsilon^{-v\frac{mv^2}{2eX}} dv, \tag{13}$$

which is the difference between two Maxwell's distributions and is not itself a Maxwell's distribution except in particular cases. The maximum value of the first term obtains when

$$v = \sqrt{\frac{eX}{m[(1+P)v - P'v']}} \tag{14}$$

and of the second term when

$$v = \sqrt{\frac{eX}{mv}}. \tag{15}$$

When there is no ionization by collision the second term in (13) vanishes and the first comes to a maximum given by equation (15). In case ionization is due entirely to electrons $P'v' = O$ and equation (13) reduces to equation (8) with the maximum given by equation (9). The most probable velocity is seen to be less than it would be if there were no ionization. This is due to the fact that those ions formed very near the plate a reach it with velocities below the average. Another particular case of interest occurs when $Pv = P'v'$, or when the positive and negative ions are equally efficient in the production of new ions. Then both terms of (13) combine to give a Maxwell's distribution identical with that found when there is no ionization. In this case the number n of electrons passing a plane in the gas in one second is the same for all positions of the plane. Only when the distance d is very small can this case be realized experimentally; otherwise an arc is set up.

B. Elastic Impact.[1]

Ionization Due Exclusively to Electrons.

The only points in which the treatment of this case differs from that in the case of inelastic impact are in the expressions for the number of electrons starting from rest in any layer and for the probability of reaching a without being stopped. We thus have $2Pnvdx$ electrons starting from rest in the layer dx each second and

[1] This treatment is only approximate, since it does not follow the new-formed electrons in their subsequent history. An exact treatment is given in the following paper.

$$Px = \epsilon^{-Pvx}.$$

Also

$$dn = -Pnvdx,$$

whence

$$n = n_a\epsilon^{-Pvx}.$$

Therefore

$$F(x)dx = 2Pv\epsilon^{-2Pvx}dx. \tag{16}$$

From equations (6)

$$F(V)dV = 2P\frac{v}{X}\epsilon^{-2P\frac{vV}{X}}dV \tag{17}$$

and

$$F(v)dv = 2Pv\frac{mv}{eX}\epsilon^{-2Pv\frac{mv^2}{2eX}}dv. \tag{18}$$

The velocity distribution again conforms to Maxwell's law and the most probable velocity is

$$v = \sqrt{\frac{eX}{2Pvm}}. \tag{19}$$

By comparison with equation (9) it is seen that the velocities are greater in the case of elastic than in the case of inelastic impact. It will be shown that this accounts quantitatively as well as qualitatively for the relatively large ionization in helium, argon, etc.

A certain amount of caution must be exercised in interpreting v in these equations. v refers always to the average number of collisions in one centimeter path in the direction of the electric force. In inelastic impact there is no motion in any other direction except the negligible amount due to the effects of thermal agitation. In the case of elastic impact, however, there is in general a considerable component of velocity perpendicular to the electric force, due to the rebound at elastic collisions. Thus the v which appears in the formulæ for elastic impact is larger than the reciprocal of the mean free path. Direct measurements of v in various gases are being made in this laboratory.

C. Ionization in a Mixture of Elastic and Inelastic Gases.

Let P_ϵ and P_i be the probabilities of ionization at an impact of an electron with molecules of the elastic and inelastic gases respectively, and let v_ϵ and v_i be the average numbers of collisions with molecules of these gases in one centimeter path of an electron. The relative magnitudes of v_ϵ and v_i will vary according to the proportions in which the gases are mixed.

Following the same reasoning as before we find that $n[(1+P_i)v_i + 2P_\epsilon v_\epsilon]dx$ electrons start from rest in the layer dx each second. $\epsilon^{-v_i x}$

is the probability of reaching a without an inelastic collision and $\epsilon^{-P_\epsilon \nu_\epsilon x}$ is the probability of arriving without having been stopped by an ionizing elastic collision. Thus

$$P_x = \epsilon^{-(\nu_i + P_\epsilon \nu_\epsilon)x}.$$

Also

$$dn = -(P_i \nu_i + P_\epsilon \nu_\epsilon) n dx,$$

whence

$$n = n_a \epsilon^{-(P_i \nu_i + P_\epsilon \nu_\epsilon)x}.$$

Therefore

$$F(x)dx = [(1 + P_i)\nu_i + 2P_\epsilon \nu_\epsilon]\epsilon^{-[(1+P_i)\nu_i + 2P_\epsilon \nu_\epsilon]x} dx, \tag{20}$$

$$F(V)dV = \frac{(1 + P_i)\nu_i + 2P_\epsilon \nu_\epsilon}{X} \epsilon^{\frac{-(1+P_i)\nu_i + 2P_\epsilon \nu_\epsilon}{X} V} dV, \tag{21}$$

$$F(v)dv = [(1 + P_i)\nu_i + 2P_\epsilon \nu_\epsilon] \frac{mv}{eX} e^{-[(1+P_i)\nu_i + 2P_\epsilon \nu_\epsilon] \frac{mv^2}{2eX}} dv. \tag{22}$$

In this case also the distribution follows Maxwell's law. Equation (22) reduces to equation (8) when $P_\epsilon \nu_\epsilon = O$ and to equation (18) when $\nu_i = O$.

Expressions for $F(v)dv$ similar to equation (13) may easily be obtained to apply to cases of elastic impact by both positive and negative ions. Since there is yet no evidence of elastic impact by positive ions it has not been thought worth while to include a discussion of this possibility.

The importance of equation (21) will be suggested in a following paper in which it will be shown that the expression for α derived from equation (21) explains the extreme electrical sensitiveness of helium and argon to the slightest traces of ordinary gases and that it accounts for the departure from theory of many experimental results.

PALMER PHYSICAL LABORATORY,
PRINCETON, N. J.

PROCEEDINGS

OF THE

AMERICAN PHYSICAL SOCIETY.

THE TRUE TEMPERATURE SCALE FOR TUNGSTEN AND ITS EMISSIVE POWERS AT INCANDESCENT TEMPERATURES.[1]

BY A. G. WORTHING.

THE experimental part of the work here reported consisted in measuring the brightness of an incandescent, hollow, cylindrical, tungsten filament perforated with small holes and mounted in a large lamp bulb. Such determinations were first made for a hole and then for the adjacent surface. The ratio of the latter brightness to the former, when corrected for the difference in temperature between the interior and the surface and for the departure from blackness of the radiation from the interior due to the presence of the small hole and any lack of symmetry in the filament temperature distribution, gives the emissive power for the substance at the surface temperature. Because the radiation from tungsten deviates from Lambert's cosine law, the emissive power has in the present work been so limited as to refer only to that radiation which leaves the surface normally.

Black-body temperatures were obtained by comparing the observed brightness, with the aid of Wien's radiation formula, with that of a black body at the palladium point. The true temperature scale consists of the relation thus found between the black-body temperature of the filament surface and that of the adjacent hole, *i. e.*, the true temperature of the filament.

A linear relation was found between emissive powers and true temperatures for the region 1200° K. to 3200° K. such that the emissive powers for the two limiting temperatures were respectively .467 and .406. The uncertainty in these values should not be much over 1 per cent. The respective corresponding differences between the red ($\lambda = .666\,\mu$) black body temperatures and the true temperatures are 33° and 375°.

Measurements were attempted on the tungsten arc much after the manner described by Langmuir. Due to large temperature gradients across the molten tungsten no satisfactory determinations could be made of the emissive power. However, it was noticed, contrary to what was concluded by Langmuir, that the brightnesses of molten and of solid tungsten at the melting

[1] Abstract of a paper presented at the Columbus, O., meeting of the Physical Society, December 27–30, 1915.

point are nearly identical. Assuming the linear relation between emissive power and temperature for solid tungsten to continue up to the melting point, it follows that this occurs at 3630° K. This corresponds to a red black body temperature of 3140° K. and an emissive power of .390.

Though the results given above are believed to be dependable within reasonable uncertainties of measurement, further verification with other filaments will be attempted previous to the publication of the completed paper.

NELA RESEARCH LABORATORY,
NATIONAL LAMP WORKS OF GENERAL ELECTRIC COMPANY,
NELA PARK, CLEVELAND, OHIO.

THE X-RAY SPECTRUM OF TUNGSTEN.[1]

BY ARTHUR H. COMPTON.

AS a source of X-rays for the examination of the spectrum of tungsten, a Coolidge X-ray tube with a tungsten anti-cathode was used. The tube was excited by means of a transformer with a rectifying device. The spectrum was analysed by means of a recording X-ray spectrometer, the intensity of the beam reflected from the crystal being determined by an ionization method with the help of a highly sensitive electrometer.

In addition to the five well-known lines of the characteristic *L*-radiation from metals, the spectra obtained verify the two new lines discovered by Barnes[2] in the spectrum of tungsten, and indicate the existence of five other lines. They also show that one of the lines which has been thought to be single is really a close double. This gives a total of 13 lines observed in the *L*-radiation from tungsten, 2 of which are, however, somewhat uncertain.

Line.	Glancing Angle.	$\lambda \times 10^{-8}$ Cm.	Barnes' Values.[1]	Remarks.
a	9° 44.5′	1.0387		
b	9° 53.1′	1.0539		Line somewhat doubtful.
c_1	10° 3.7′	1.0725	1.082	Very close.
c_2	10° 7.7′	1.0796		Double.
d	10° 25.7′	1.1107	1.113	Strong.
e	11° 36.3′	1.2349		
f	11° 49.9′	1.2587	1.258	Strong.
g	12° 0.4′	1.2771	1.277	
h	12° 11.4′	1.2962	1.296	Strong.
i	12° 22.7′	1.3160	1.312	
j	12° 44.7′	1.3543		Line uncertain.
k	14° 4.7′	1.4933	1.477	Moseley gives 1.486.
l	14° 11.1′	1.5044		

[1] Abstract of a paper presented at the New York meeting of the Physical Society, February 26, 1916.

[2] J. Barnes, Phil. Mag., 30, p. 368, 1915.

The wave-lengths of these lines have been determined by reflection from a cleavage plane of calcite. The angles and corresponding wave-lengths are given in the accompanying table. The probable erro rin the observed angle for the more intense lines is less than $\pm$ 0.5′, but for the fainter lines is somewhat greater.[1]

PALMER PHYSICAL LABORATORY,
PRINCETON UNIVERSITY,
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NOTE ON THE END EFFECT IN THE ELECTROSTRICTION OF CYLINDRICAL CONDENSERS.[2]

BY EDWIN C. KEMBLE.

THE electric field in the neighborhood of the ends of the coatings of a cylindrical condenser exerts a longitudinal traction

$$P = \frac{ad\delta_2 H^2}{4}$$

by direct action on the dielectric. Here,

a = internal radius of cylinder,
d = thickness of cylinder,
H = average electric force,
δ_2 = constant depending on the change of the inductivity of the dielectric by strain.

There is also a force exerted by the electric field on the edge of the coating. Its value is

$$P^1 = \frac{ad\,K\,H^2}{4}$$

where K is the inductivity of the dielectric.

By taking these forces into account we can bring the formulas for the elongation of charged cylindrical condensers derived by Sacerdate[3] by the "energy method" and by Adams[4] by the "elasticity method" into complete agreement. The discrepancies are explained both for the case of adherent and for that of non-adherent coatings.

HARVARD UNIVERSITY,
CAMBRIDGE, MASS.

[1] Note added March 30, 1916: The wave-lengths given in this table are calculated using for the distance between the layers of atoms in calcite the value 3.0695×10^{-8} cm. As will be explained elsewhere, this grating space is rather 3.0279×10^{-8} cm., so that the wave-lengths here given should be divided by the factor 1.0135.

[2] Abstract of a paper presented at the New York meeting of the Physical Society, February 26, 1916.

[3] Journ. de Phys. [3], 8, p. 457, 1899, and [3], 10, p. 196, 1901.

[4] Phil. Mag. [6], XXII., p. 889, 1911.

ON POSSIBLE PLANETARY MAGNETIC EFFECTS.[1]

BY L. A. BAUER.

THE question of the existence of cosmical effects arising from possible planetary magnetic fields is one engaging the attention at present of various investigators, especially of astronomers. For example, it has been known for some time that there are certain irregularities in the motions of the moon too large to be accounted for apparently by any known outstanding gravitation effects. Similar irregularities are shown by the motions of Mercury, Venus, and the earth. It therefore becomes a matter of interest to ascertain, if possible, whether these irregularities in the motions of astronomical bodies can be associated, in any way, with magnetic effects. Accordingly, as a first step, a preliminary formula has been theoretically established for determining the field strength of possible magnetic fields enveloping the members of our solar system for which certain requisite constants are known. Let M_e represent the strength of the earth's magnetic field at its poles, namely, about 0.65 of a C.G.S. unit, and let ω_e, R_e, D_e, G_e represent, respectively, the earth's angular velocity of rotation, mean radius, mean density, and gravity at the surface. Give similar significance to the quantities, M_a, ω_a, R_a, D_a, G_a for any rotating astronomical body (a). Then we may have approximately: $M_a : M_e = (\omega_a R_a^2 D_a) : (\omega_e R_e^2 D_e) = (\omega_a R_a G_a) : (\omega_e R_e G_e)$. If, for example, the astronomical body (a) is the sun (S), we get a field strength (M_s) which agrees within about 10 per cent. of Hale's provisional value $(80 M_e)$. For the planets Mars, Jupiter and Saturn, whose angular velocity of rotation is known, we get: $M_m = 0.2\ M_e$; $M_j = 68\ M_e$; $M_s = 24\ M_e$. It thus appears that, on the hypothesis underlying the formula, Jupiter, Saturn, and probably also Uranus and Neptune, may be enveloped by stronger magnetic fields than is the earth. An interesting numerical equality (within about 10 per cent.) was found to exist between the products (ωv), ω being the angular velocity of rotation and v the orbital velocity, in the case of the four planets (Earth, Mars, Jupiter and Saturn) for which both quantities are definitely known.

[1] Abstract of a paper presented at the New York meeting of the Physical Society, February 26, 1916.